PHYSICOCHEMICAL STUDIES ON SILICIOUS DUSTS: SURFACE STRUCTURE AND RELATED PHENOMENA.

by

JOHN G. GIBB, B.Sc., A.R.T.C., A.R.I.C.

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Technical Chemistry Department,
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Glasgow, C.1.

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S Y N O P S I S.

(1) Various important theories on the mechanism of the toxic reaction of inhaled silicious dusts are described in the Introduction. The Solubility Theory of silicosis, in particular, has stimulated research on the surface structure and properties of silicious dusts, and some recent results are discussed in the light of this concept.

(2) An analytical method for the estimation of silica in solution is described, and the validity of the method is justified by comparison with results of recent investigations on the combination of silicate and molybdate ions.

Changes in surface structure brought about by removal of the surface layer from crystalline quartz and fused-silica dusts by 40% hydrofluoric acid, and from Lochaline sand dust by a borate buffer (pH 7.5), are studied by electron-optical methods. The accompanying changes in electron-diffraction pattern show that the original surface layer is amorphous (estimated mean thickness 0.03 - 0.06μ); for quartz and Lochaline sand dusts there is some evidence of an inter-:mediate layer of very minute crystallites between the amorphous layer and the crystalline core.

(3) The rate of solution of a pure rock crystal dust (e.g. Madagascar quartz) in a borate buffer (pH 7.5) is reduced by prior extraction with acid, whereas similar treatment of impure silicious dusts (e.g. Lochaline sand , a sandstone or orthoclase felspar) increases their solubility rates. The /

/enhanced rate is not due to regeneration of a disturbed amorphous layer of the type produced by crushing and grinding silica; and it can be reduced, sometimes back to its original value, by heat treatment within the temperature range ca. 60 - 1150°. The observed enhanced rates cannot be attributed to hydration of the silica surfaces during acid extraction. During reduction of the enhanced solubility rates by heat treatment, and by other methods (described), the silica sur-:faces become inactivated and further extraction with acid does not raise the solution-rate again.

Pre-treatment of such dusts with sulphuric acid of various pH values causes an increase in all initial pH values, indicating partial removal of hydrogen ions from the extracting medium. It is considered that these ions are adsorbed on the surface irregularities produced by the removal of alumina (demonstrated) and other impurities during acid treatment; the various solubility effects observed are explained on the basis of this layer of hydrogen ions.

Reduction of solubility by heat treatment shows the characteristics of a second-order reaction. It is suggested that the reaction consists of desorption of hydrogen ions; a tentative mechanism is discussed.

(4) Adsorption of a basic dyestuff (Methylene Blue) on the surface of silica dusts, with and without the disturbed layer produced during crushing and grinding indicates that for

/Lochaline sand, pure quartz, and vitreous silica the layer is more active than the core in sorption processes, just as in solution processes. Acid extraction of an impure silica dust effectively reduces the equilibrium adsorption, the pH of the extracting medium being a factor controlling the extent of this reduction; and a similar reduction is again apparent when an acid-extracted dust is heated. These results support the conclusion that the increased solution-rate produced in a silicious dust by acid treatment is due to the adsorption of hydrogen ions on the particle surfaces.

(5) It has been shown that the disturbed layer gene-:rated on the surface of silicious dusts by a quartz polishing agent is similar to the disturbed layer produced by grinding. The activity of the former layer in solution processes is dependent on the nature of the substrate. An electron-optical study of such surfaces shows that the layer produced by polish-:ing is amorphous and that some particles of polishing agent become fragmented during the process.

The possibility of recrystallising the amorphous layer on silica dust surfaces in order that the total free silica content might be estimated accurately by differential thermal analysis is discussed and has been investigated. Devitrification by heat occurs to an extent which is not statistically significant, precluding the use of this method in its present form for differential thermal analysis.

INTRODUCTION.

'Pneumokoniosis' is a generic term representing the common types of dust disease. Silicates have been found injurious to health and other dusts have a detrimental effect under certain conditions. Siderosis, for example, is a diseased condition of the lungs of metal workers, particularly in iron or iron ores. Asbestosis is a lung disease caused by breathing asbestos dust. The dust of free silica is considered more dangerous than other dusts, chiefly because its victims are thought to be more susceptible to the action of tubercle bacilli than persons exposed to non-silicious dusts. Silicosis, as it is called, is a disease of the lungs arising from the inhalation of airborne silicious dusts produced in mining operations and other industries where stone is ground. The following definition was adopted at the International Silicosis Conference in South Africa in 1930 :

"Silicosis is a pathological condition of the lungs due to inhalation of silicon dioxide. It can be produced experi-:mentally in animals".

Peculiar discoloration of coal miners' lungs was observed by doctors throughout the coal mining districts of east and west Scotland, but until 1831, no recorded infor-:mation is available which attempts to relate this lung con-:dition to occupation. Gregory[1] was the first author to observe that this particular lung condition arose out of employment in coal mines. Probably the earliest recorded information about the symptoms of silicosis was made by /

/Diemerbroek. He was reported[2] to have made in 1649 the first section of a stonecutter's lung, which, in a case of fatal asthma, revealed "lung vesicles completely clogged with fine dust." As quoted by Ramazzini[3], he found large heaps of sand, and while cutting the lung vesicles, he thought he had encountered some sandy body. Thackrah[4], in 1832, noted that different types of dust had widely different pathogenic properties, and an examination of the expectation of life in various dusty trades in Britain revealed that the incidence of the disease was high in sandstone quarries and low in brick and limestone factories.

Peacock[5] and Greenhow[6] recognised the presence of hard, gritty particles in lung sections and Peacock made the distinction between dust phthisis and pulmonary tuberculosis. Physicochemical evidence was obtained by Greenhow, using polarised light, that the lungs of metal grinders contained a proportion of fine silica particles.

In a report by Collins[7] in the 1915 series of Milroy Lectures, devoted to industrial pneumokoniosis, he states his experience that some dusts, such as coal, are not only appar-:ently innocuous but may even inhibit phthisis. Most air-:borne dusts have an injurious effect, but silica is the most harmful. Thus, the idea of noxious dust was bound with free crystalline silica and silicosis.

Theories on the cause of Silicosis.

Mechanical Theory. /

Mechanical Theory.

The mechanical theory of the disease was evolved from experimental results obtained by Haldane[8] in 1915 while investigating the pathogenicity of materials used for stone dusting. Soft materials, such as chalk and clay, were shown to be harmless, while granite, flint, and other hard materials produced inflammation of lung tissue. There were some doubts, however, as to whether such small dust particles were harmful by virtue of laceration of tissue with subsequent lung disa-:bility. This theory was gradually abandoned and supplanted by the chemical theory.

Chemical Theory.

Lanza[9] observed that dusts containing the greatest amounts of silica were the most active and that pneumatic drilling machines, producing airborne dust of 2 - 5μ in size, or less, increased the incidence of lung disease. It was shown by Gye and Kettle[10] that subcutaneous injection of silica in animals produced a lesion characteristic of the material. Tubercle bacilli were also found to proliferate in the necrotic areas surrounding the particles. These observations marked the real beginning of the chemical concept. Gardner's classical experiment in 1923 finally ousted the mechanical theory[11]. He observed that, although silicon carbide particles were very sharp and abrasive, they did not produce silicotic nodules in the lungs of experimental animals; diffuse fibrosis

/was observed. Research work was now directed towards accumu-:lation of evidence that the pathogenic nature of a mineral dust was in some way connected with its chemical composition.

Gye and Purdy[12] were successful in producing necrosis in the liver of mice by injections of colloidal silicic acid. Following the work of Gardner, Sayers[13] produced some evidence that mineral dusts containing a high percentage of free silica were the most active, and that their hazardous nature could be attributed to a poisonous action on dissolution in the lung fluids. Another record of this importance of the presence of mineral matter in airborne dust is given in observations made by Muir[14] during 3,000 necropsies. He testified that black lungs, encountered in coal miners, were benign, and that he had not met fibroid phthisis in the coal industry as he had done in his wide experience of masons' lung disease. In his opinion, coal dust, unless mixed with rock dust, was harmless.

A subsequent report by Heffernan[15] apparently con-:tradicted the chemical theory. He investigated the condi-:tions under which Derbyshire gannister bricks were made. Although the raw material had a high free silica content (84% silica, 16% clay and earth, some organic matter) the workers did not contract silicosis. He concluded, however, that the non-silicious components of the mixture were exerting some influence on the pathogenic nature of the free silica.

An earlier record of this phenomenon of toxicity /

/suppression is found in a "Note on Anthracosis" in which Smart[16] confirmed his view that pulmonary consumption was extremely rare among coal miners. He suggested that operations in the coal industry must possess a protective feature not common to other dusty trades. He says, "The preserving element may, after all, be the dust derived from the coal, which has hitherto been credited with the opposite effect."

At the time when Hefferman's apparent contradiction appeared, Kettle[17] suggested a concept which indicates that silica is leached from the inhaled particles by the lung fluids and dissolves therein as 'colloidal' silicic acid which acts as a cell poison producing necrosis, inflammation, and des-:truction of fibrous tissue. He concluded that the growth of tubercle bacilli was promoted by the silica particles themselves (and not by the fibrous tissue) by injecting a definite quantity of fine silica particles beneath the skin of one flank of a white mouse, and in the opposite flank, the same quantity of aluminium oxide particles. A large dose of tubercle bacilli was then injected ~~with~~ into the tail vein of the animal. The blood stream distributes these bacilli uniformly to all parts of the body, but after several days, large masses of them were found at the site of the injected silica, indi-:cating that the reaction induced by silica produces a favour-:able medium for the growth of tubercle.

Another mechanism for the pathogenic reaction of

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/finely divided silica was proposed by Heffernan[18]. He visualised that the particles became engulfed in phagocytes in the alveoli and were then carried into the pulmonary lymphatic channels. The silica particles within the phago-:cytic cells cause destruction of these cells, leaving a "ghost" of cell wall; this reaction spreads to other cells. He proposed that the death of these cells was due either to the formation of 'colloidal' silicic acid after hydration of the particles by the cells, or to adsorption of some consti-:tuent of the cell protoplasm on the particle surfaces.

Further work on the chemical theory was carried out by Kettle[19] to determine the relative toxic effects of various silicious and non-silicious dusts. By examining tissue reactions in mice and rabbits injected subcutaneously, he concluded that the silicious dusts quartz, shale (35% silica), kaolin, and asbestos were highly toxic, while the non-silicious dusts alumina, iron oxide, coal, and marble were inert. He also confirmed his earlier findings that the silica dusts aided in the growth of tubercle bacillus while the other dusts did not. Perhaps the most striking experiment in this part of his work was the coating of a very active quartz with a thick layer of iron oxide giving a dust containing 59.9% silica and 40.1% iron oxide. This was then found to be an inactive dust, and he postulated that the innocuous nature was due to the coating of oxide preventing dissolution of the silica.

In the following year, Policard[20] produced further evidence that the pathogenicity of a dust was in some way connected with its solution properties. He found that if cells are poisoned by silica in solution they do not disintegrate and disappear as do other cells. They tend to preserve their structure as if "mummified". He suggested that the pathogenic nature of a silica dust is governed by its ability to produce silica in solution in body fluids.

Solubility Theory.

From the combined efforts of these workers, the solubility theory of silicosis was gradually evolved. King[21] has carried out extensive experiments in this field and his results, in general, support the concept. Quartz and flint yield silica in solution at the greatest rates and are the most active. Shales and mica, on the other hand, have very low solution rates and are the least harmful. Most mineral silicates, moreover, are less soluble than the free silicas. Kaolin, for example, has a very low solubility. When admixed with quartz it would be expected, as pointed out by King[22], that the silicic acid yielded in solution would depend on the most active member of the mixture and when in excess, the solubility would tend to approach that of quartz. It is significant that the solubility of quartz is reduced from 9 mg./100 ml. to about 1 mg./100 ml. when mixed with stone dust containing naturally occurring kaolins. These depressions of solubility

/might well explain depressions of physiological activity.

Further evidence in support of this theory is found in results obtained by Denny, Robson and Irwin[23], who showed that if a quartz-laden atmosphere contained small amounts of finely ground metallic aluminium, development of a fibrogenic reaction in the lungs of animals exposed to such an atmos-:phere could be prevented. The presence of aluminium powder was also shown to decrease the solubility of the quartz. The reaction mechanism was investigated by these workers in a very interesting manner. Quartz pebbles from a tumble mill were exposed, in distilled water, to the action of metallic alumi-:nium powder. After some weeks, the pebbles were scrubbed clean and it was found that they could be stained pink with aurine tricarboxylic acid, indicating that adsorption of aluminium hydroxide had taken place, the effect of this layer being similar to that of the iron oxide in Kettle's experi-:ment. The adsorbed layer, after drying, gave an electron diffraction pattern corresponding to the crystalline α-alumina monohydrate. It is thus highly probable that the film on the quartz is a gelatinous hydrated oxide of alumina, which is converted into the crystalline monohydrate on drying, the drying process being necessary since electron diffraction patterns must be taken in vacuo. Experiments also showed that the crystalline modification did not stain deeply enough with aurine to account for the observed colour, while precipi-:tated gelatinous oxide becomes deeply stained.

During experiments of a similar nature, Belt and King[24] were unable to repeat these observations using the technique of intratracheal injection. It was suggested, however, that the aluminium metal was very quickly eliminated in the body processes without exerting a depressant effect. In a later series of experiments[25] these workers were successful in substantiating the results of Denny et al. The method of dust administration was found to be the controlling factor. By exposing rats to an atmosphere of quartz containing 2% of aluminium, a retardation and possibly a prevention of the development of silicotic lesions could be achieved.

The solubility theory, although successful in explaining the in vivo mechanism of the disease, does not always hold good in practice. For example, Gardner[26] found that a very finely divided silica, produced as a condensate from the furnaces of a silica-ware factory (20 Angstrom silica) does not affect the lungs or liver of experimental animals, although it is extremely soluble. He suggested that this was due to rapid elimination in the body before it could become toxic. King[21] observed that if this fine amorphous material were injected into animals in large amounts the result was fatal, small doses producing no fibrogenesis.

During extensive research on the solubility of dusts from South Wales coal mines, King[27] found no marked difference in the solubilities of dusts of known difference in patho-

/:genicity. Shales and sandstones from these mines contain varying amounts of quartz, mica, and kaolin, but their solu-:bilities are very low and very similar. Silica solubility of dusts and powdered strata from bituminous mines (low incidence of silicosis) and anthracite mines (high incidence) showed little difference and he concluded that there must be some difference between the dusts, accounting for the variation in pathogenicity, which has escaped detection. The low solu-:bilities of the dusts could be accounted for by the release of aluminium from other constituents forming a protective coating of alumina round the silica particles. It may well be that this coating disappears in the alveolar spaces and lymph tissues leaving the particles to exert their toxic effect.

Freshly-fractured Surface Theory.

Another theory of silicosis which has greatly influenced research emphasises the importance of freshly ground dust in the production of the disease. In 1935, Heffernan[28] suggested that silica was biologically active by virtue of the presence of unsatisfied valencies at the particle surfaces. Satisfaction of these valencies could take place by hydration in the atmosphere; to support this theory he had to postulate that only freshly-fractured material was active. There is further evidence in support of this postulate in the results of Briscoe, Matthews, Holt and Sanderson[29] who found the biological reactivity of very fine dust to be much less

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/after atmospheric exposure than that of a similar freshly-formed dust. They suggest this as a possible "explanation of the failure of attempts in the past to induce silicosis in animals by exposing them to artificially raised dust clouds." In 1937, Brammall and Leech[30] proposed a concept which stated that harmfulness of dust may be in some way related to surface area. Newly formed dusts are more pathogenic than dusts whose fractured surfaces have been weathered, or have undergone some similar transformation. The results of Kitto and Patterson[31] afford evidence that the surfaces of dust particles alter in some way which, during ageing, causes a decrease in solution potential. In order to obtain comparable results for solubility data of various dusts, the ground materials must be used at the same interval of time after the actual grinding, since the rate of solution decreases with the time which has elapsed since grinding. In the classical experiment of Denny et al. already mentioned[23], silicosis was produced much more readily by exposing animals to freshly-formed quartz dust than by exposing them to "stale" dust.

Gardner[32] had previously found, in 1932, that a commercial silica dust, after many years storage, did not fail to be as active as it had been previously. Despite such defects, the freshly-fractured surface theory was still upheld and was re-introduced in 1947 when Policard[33] quoted the following examples :

1) Sheep in the North African desert did not develop silicosis because the sand there was not freshly-fractured, but weathered.

2) Sandblasters develop the disease because, although they are exposed to weathered dust, the dust is fractured by heat and impact.

This 'desert sand' theory was ousted by Heywood[34] when he cited the results of Bagnold[35], which showed that most of the particles in this sand are greater than 200-mesh size. The airborne dust breathed by the sheep comes from adjacent land and contains practically no silica. The fact that the sandblasters were exposed to very fine particles is sufficient to account for the occurrence of the disease.

Policard[36] later put forward evidence which showed that besides these large dust particles, fine material of the order 3μ in size is found; this latter dust results from the weathering of the larger particles. In contrast to the sand, the fine silica dust passes the respiratory tract and reaches the alveoli, a fact which is supported by histopathological observations. In the lungs of four deceased inhabitants of Sahara, no silicotic lesion of any type was found, and dust particles had accumulated in the periarterial and peribron-:chial sheaths. Silicon was found to be present in the masses of dust particles, and the Debye-Scherrer X-ray dif-:fraction method indicated the presence of quartz in some, but gave doubtful results in others owing to the small amount of

/silica present. Policard also showed that this fine dust (2 - 3μ) produces in experimental animals a reaction similar to that of innocuous substances, such as carbon, although X-ray diffraction showed the presence of quartz in the injected dusts and in the peritoneal nodules.

These observations are in support of the concept already outlined. The sand dusts are 'old' dusts constantly in motion and subject to severe weathering. The innocuous nature of these dusts may be explained, on the other hand, by assuming the impurities to exert a depressing effect. The main impurity is iron oxide ($Fe_2 O_3$) which has been shown by Haldane[37] to reduce the toxicity of associated silica particles. These results again indicate the importance of this concept.

Atomic Oxygen Theory.

A similar theory has been proposed by Weyl[38], who has adduced evidence that freshly ground silica is biologically active because of the presence of atomic oxygen at the particle surfaces. This effect is greater with clay, but it has been found that clay may retard or even prevent the production of silicosis. Wright[39] has extensively discussed this theory and summarises the important biological properties of silica as follows :

1. Crystalline and amorphous silica produce pathological changes, culminating in fibrosis, when injected into animal tissue. These reactions are unlike those of any other mineral which has been investigated.

2. The upper limit of particle size must be about 3μ in order to produce these changes; the lower limit, however, is not so well defined, but in general a value of 100 Å is accep-:ted. Colloidal silica is known to be very toxic, but the reaction is not easily distinguished from that produced by other substances.

3. That this activity is governed by surface properties is shown by the following considerations.

a) It is only shown by particles within a certain size range.

b) The effect of a given weight of silica is proportional to the fineness of the particles of which it is composed.

c) There is no apparent loss of material.

d) It is inhibited by such substances as iron and aluminium which may be adsorbed ~~on~~ to the surface of the silica.

4. Growth of tubercle baccilli is promoted by silica in animal tissues. Other necrotising substances do not possess this property.

5. It appears from the evidence obtained up to the present that silica acts as a tissue poison rather than a cell poison.

'Overloading' Theory.

There is some evidence that mere overloading of lungs with dust is a causative agent in the production of fibrous tissue. During an extensive research programme carried out by the Medical Research Council, it was concluded that, since the quartz content of airborne dust was seldom greater than 4%, overloading of the workers' lungs with this coal dust may be an

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important factor. Gough[40] also emphasised that the main result in this particular type of pneumokoniosis was not the production of fibrous tissue, but a change known as focal emphysema, and he suggests that this may be an effect of dust accumulating in the lung, and exerting a mechanical interference with normal functioning of the lung. He also reported that the "coal nodule" is the earliest lesion in the lung due to breathing of coal dust. In the region of such nodules (collections of dust), this focal emphysema is developed. According to Gough, there are actually two diseases which contribute to coal workers' phthisis - (a) "Simple pneumokoniosis" caused by accumulation of coal dust, the latter being responsible for only a small amount of reticulin fibrosis, (b)"Infective pneumokoniosis" due to the combined action of tubercle and coal dust. Infective nodules consist of collagen-like fibrous tissue which later combine to form "massive fibrosis".

In the same year, Heppleston[41] gave a detailed report on the development of the coal nodule, and his views on the change described by Gough as focal emphysema. More recently, he has recorded evidence that the fundamental lesion of coal pneumokoniosis is the same in workers all over the world; he concluded, as did Gough, that dust accumulation rather than any physical or chemical activity of silica was the causative agent in simple pneumokoniosis. It has been suggested by Fletcher[42] that this latter stage becomes critical when

/progressive massive fibrosis appears and that if workers were removed from dusty areas before this stage appeared future health would be protected. Cochrane, Davis and Fletcher[43] have suggested that if a worker be removed from a danger area when only slightly affected by simple pneumokoniosis, then progressive fibrosis will probably not result. If he is more acutely affected, however, further development will not likely ensue whether or not he is removed to a healthy atmosphere.

In 1947, it was stated that this concept of over-:loading of lungs with dust was gradually supplanting the solution theory[44]. Jones[45] pointed out that, about 15 years ago, a dust containing less than 50% free silica was thought to be harmless, and now anthracite dusts containing less than 2% free silica are responsible for about 80% of the fibrosis in this country. In spite of these considerations, the solu-:bility theory of silicosis is apparently favoured by the majority of workers in this field.

Sericite Theory.

In 1933 an interesting thesis was propounded by Jones[46], in which he defined sericite as the causative agent in the production of silicosis in lung specimens investigated. He examined a series of human lungs with the petrological microscope and related the residues in the lung ash to the geological composition of the materials which had caused the disease. In a later publication he emphasised the fact that for every grain of quartz in these lung residues there are

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/present hundreds of mineral fibres. He further defines this in the following statement[47]:

"The mineral residues obtained from the 29 silicotic lungs of employees who had been engaged in the various indus-:tries in this country consist, therefore, mainly of myriads of minute acicular fibres of sericite". In spite of this, Jones did admit that in some exceptional cases, free silica might be the responsible agent. He also made an interesting comparison of the high incidence of silicosis in South Wales and the low incidence in Scotland, and attributed the high incidence in the former coalfields to the presence of sericitic fibres, while "..... the Scottish sandstones contain very few such fibres and, indeed, compared to the myriads present in South Wales rocks, fibres of sericite in these Scottish rocks are rare".

This sericite theory was widely discussed throughout the world and, in general, the hypothesis was accepted. Haldane[48], however, criticised it and emphasised that he had found nothing to indicate that either the presence or absence of sericite had anything to do with the silicosis produced by quartz, whereas there was an overwhelming amount of evidence pointing to dust which contained a high percentage of quartz. He explained the presence of sericite in the lung as due to the gradual dissolution of free silica in an alkaline liquid, compared with the more difficultly soluble natural silicates. Commenting on this theory, King[27] stated that high solubility/

values obtained for sericite may have been due to certain treatments given to the dust before use, and that any alteration in the chemical properties of a dust will undoubtedly change its effect on tissue.

The sericite hypothesis is not now generally accepted, nor does it appear to have been proved by animal experiments, and more recent years have shown that many mining areas outside South Wales produce many cases of the disease.

Importance of Particle Size.

It is interesting to consider briefly the limits of particle size thought to be most harmful to lung tissue. It was shown by Drinker in 1925[49] that about 53% of particles (distribution by size-frequency) in phagocytic cells were of 1 or 2μ in diameter. Particles above 5μ are very rare in dust cells. Some more recent work by Schulz and Tebbens[50] supports this conclusion, and indicates that silica dusts of 3μ and less are of the greatest pathogenic significance. These workers prepared 4 specimens of flint dust (99% silica) having mean particle sizes of 3.3, 1.7, 1.0, and 0.6μ. Animal experiments were carried out, nine rabbits being used for each dust sample. Each animal received 400 mg. of dust injected in two equal doses at 2-month intervals. One rabbit was killed from each group at intervals of 3 days to 17 months. It was found that the degree of fibrosis produced increased with decreasing particle diameter, the smallest particles producing a marked degree of injury

/compared with those having a mean size of 3μ .

Using electron-optical methods, Watson[51] found that the particle sizes of dusts produced by drilling and blasting are remarkably similar when particles above 0.2 are con-:sidered (0.2μ is the limit of light field microscopy). Below 0.2μ it has been shown, using the electron microscope, that there exist more than four times as many particles less than 0.1μ in dust produced by drilling as in dust produced by blasting. It is also worthy of note in this connection that Sharpe and Hounam[52] found an examination of airborne dust from six different collieries revealed that at least 75% by number of particles visible in the electron microscope were less than 0.2μ and thus invisible in the light microscope. Examination at high magnification revealed no particles less than 200 $\mathring{A}$.

Some Recent Results.

The modern solubility theory has stimulated research in the physicochemical aspects of the dust problem, and at the present time many workers are engaged in this field. Kitto and Patterson[31], for example, while studying the solution-rates of various silicates, found that these were greatest during the initial stages, and concluded that the effect of grinding quartz is apparently the formation of more of a "highly soluble outer layer". Results obtained by Barrer[53] show that the permeability of fused silica to certain gases decreases with time of heating and initial values can be

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/produced again after etching the material with hydrofluoric acid. He concluded that this drop in the diffusion rate is due to the presence of a surface layer. The change in rate is also independent of gas purity and the rates for hydrogen and helium are decreased by the presence of silicates indi-:cating that resistance to gas penetration is due to "crystalline development in the surface layers".

By observing changes in the solubility of a silica dust brought about by pre-treatment with solution containing different anions, Clelland, Cumming and Ritchie[54] concluded that there exists on silicious dust particles an outer layer of higher solubility than the core. Their conclusions were further supported by extractive solubility experiments on quartz and natural sand dusts, both materials giving a high initial solution-rate corresponding to the dissolution of a highly soluble outer layer. During these experiments, it was observed that colloidal silicic acid was liberated in the solvent medium from five dusts examined in this way, but was only present in appreciable amounts during the initial solution periods, indicating a possible connection with the outer layer.

Clelland and Ritchie[55] also observed that this layer, after removal with solvents, could be regenerated by a purely mechanical polishing treatment using a fine rock crystal dust or fine particles of silicon carbide. Evidence was adduced that a disturbed vitreous surface layer, closely

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/associated, and perhaps identical, with the classical Beilby layer, is produced during crushing and grinding operations. The regenerated layer again yields silica very largely in a flocculent colloidal form. It has not yet been established, however, that this layer is similar to that produced by grinding. Dempster and Ritchie[56,57], using the technique of differential thermal analysis confirmed that the disturbed layer on quartz particles is amorphous, and a similar con-:clusion was reached by Nagelschmidt, Gordon and Griffin[58], using a densitometric X-ray-diffraction method.

It is apparent from the foregoing resume of investi-:gations in the field of silicosis research that a thorough understanding of the physicochemical behaviour of silicious dusts is necessary as a prelude to true physiological activity. The problem is made increasingly difficult by the complex nature of industrial dusts, in particular mine dusts, and it seems logical to confine part of the extensive programme to research with pure materials, in the hope that any knowledge gained will be of great assistance to workers in other related fields, such as medical research in experimental silicosis, or reduction of underground atmospheric dust concentration by spraying. The present work, therefore, is intended as a contribution to all aspects of research in this complex field, and it attempts to clarify our present knowledge of the sur-:face structure of silicious dusts and the solution and sorp-:tion phenomena occurring at such surfaces.

PART 1.

A. THE SOLUBILITY OF SILICA.

B. ELECTRON-OPTICAL EXAMINATION OF FINELY GROUND SILICA.

A. The Solubility of Silica.

Introduction.

The solubility theory of silicosis has led to investigations of analytical methods for the estimation of silica in solution. In earlier years the apparatus was very inadequate and results inaccurate. The main source of error lay in the methods whereby separation of solid and liquid phases was effected. The solubility values obtained by Lenher and Merril[59], for example, were subject to such an error, their results being high owing to gravimetric esti-:mation of solid particles as well as dissolved silica. Phase separation was carried out by filtration, the medium being incapable of giving a complete separation. Modern techniques, such as centrifuging and ultra-filtration, have obviated this difficulty and errors are greatly reduced. It is now possible to obtain true solutions of silica completely separated from finely-divided matter.

The 'solubility' of silica, however, is a very vague term and results depend on experimental condition, such as particle size of the solid, time of contact of solid and liquid phases, ratio of mass of solid/volume of solvent, and temper-:ature and pH of the solvent[60]. Thus, comparative solubility results must be obtained under constant experimental conditions. Gravimetric methods for the estimation of dissolved silica have now been largely replaced by colorimetric methods, these latter

/depending on the reaction between dissolved silica and ammo-
:nium molybdate in solutions of suitable pH values. Yellow silicomolybdic acid is formed, which may be further reacted with a suitable reducing agent to form a blue complex, the colour of which is compared to that given by a standard silica solution.

Experimental Conditions.

In vivo conditions were simulated as far as possible in the laboratory, so that the leaching of silica in the test-tube is similar to the process in a silica-laden lung. The fluid used was a borate buffer (described by Clelland et al.[54]) having a pH of 7.5, approximately that of lung fluids[61]. The composition of this solvent is such that it does not contain chloride or phosphate ions, these latter having been found to interfere with the colorimetric method of analysis[62,63]. The temperature was maintained at 37° (normal body temperature) in an air thermostat, within which a shaft rotated at 30 r.p.m. Cellulose acetate tubes of 50 ml. capacity (Lusteroid tube[64]) containing the solid and liquid phases were clipped to this shaft and the materials kept in continuous agitation. These tubes, employed throughout the solubility experiments, eliminate errors otherwise due to dissolution of silica from glassware.

The mass/liquid ratio was constant during estimations from which comparative solubility results were required. Some departures were made from the normal ratio of 4g./40 ml. (e.g. for dusts of very small particle size, giving high /

/solubility values) for convenience in estimating large amounts of dissolved silica. The ideal time of contact of dust and solvent is about 1 week, but in order to expedite determinations and obtain comparative results, this was reduced to 48 hours in most of the experiments.

Estimation of Silica in Solution.

The method adopted was a development[54] of the molyb-:denum-blue method of Isaacs[65], King[63], and Harrison and Storr[66]. At suitable pH values, ammonium molybdate reacts with silica in solution to form yellow silicomolybdic acid. This colour intensity is proportional to the concentration of dissolved silica and may be recorded in a calibrated absorp-:tiometer. Reduction of this acid under standard conditions, however, gives a blue complex, the intensity of which can be recorded as with the yellow solution. This latter step renders the method much more sensitive and suitable for solutions of low silica content.

The following standard reagents were used :

(i) Borate Buffer.- 11.16 g. of boric acid (A.R.) and 1.81 g. of sodium borate decahydrate (A.R.) are dissolved in 1 litre of distilled water.

(ii) 5% Ammonium molybdate. - 20 ml. of 6 N H_2SO_4 is added with stirring to a filtered solution of 6 g. of ammonium molybdate $[(NH_4)_6 Mo_7 O_{24} \cdot 4 H_2O]$ in 100 ml. of distilled water.

/(iii) Reducing solution. - 6 g. of sodium sulphite ($Na_2 SO_3 . 7H_2O$) and 1 g. of hydroquinone are dissolved in 50 ml. of distilled water.

In a typical estimation, 4 g. of dust is weighed into a Lusteroid tube and 40 ml. of borate buffer added. This is rotated in the thermostat at 37° for, say, 48 hours. With materials of large particle size, separation of solid and liquid phases was by gravity alone; with very fine dusts, however, this was effected by centrifuging at 3,500 r.p.m. for 10 minutes, followed by filtration through a Ford Sterimat filter pad (Grade SB) if the solution was turbid. The pro-:cedure of centrifuging at this moderate speed, although insufficient to effect a complete separation, was used to expedite filtration by preventing the formation of a secon-:dary filter of small particles on the filter pad. This latter filtration procedure has been shown to have no effect on the amount of silica in solution which will react with ammonium molybdate under the conditions described[54].

25 ml. of supernatant liquid is pipetted into a Lusteroid tube and made up to 43 ml. with distilled water. 2 ml. of molybdate solution is added, the solution stirred for 30 seconds, and the yellow colour of the silicomolybdic acid allowed to develop for 4.5 minutes. 5 ml. of reducing solution is added, the solution stirred for 30 seconds, and the colour of the molybdenum blue complex allowed to develop

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/for a further 30 minutes; and the intensity is read on a calibrated photolectric absorptiometer. The EEL instrument[67] was used throughout this work, incorporating a red filter (Ilford No. 608).

All reagents were measured out in a series of test-tubes equally spaced on a rack so that molybdate and reducing agent could be added simultaneously to test solutions similarly placed, and contained in Lusteroid tubes, on another rack. Stirring was carried out using a number of corres-:pondingly-spaced spatulas on a wooden block. This technique ensures constant analytical conditions and hence increased accuracy. With fine silica dusts it was found convenient to reduce the mass/liquid ratio, as already explained, so that dilution of the molybdenum-blue complex was not required. This latter procedure would, of course, introduce a source of experimental error and decrease the accuracy of the method.

Recent Research on the Combination of Silicate and Molybdate.

It has been shown by Strickland[68] that pH is not the sole factor in silicomolybdate formation. He concluded that it is inadvisable to consider pH without reference to the quantity of molybdate or other electrolyte present, and he recognised two forms of silicomolybdic acid. If the molyb-:date, present as the ion $MoO_4^{''}$, is acidified with up to 1.45 - 1.50 equivalents of acid per gram-ion of $MoO_4^{''}$, then the main product of the reaction is the silicomolybdic acid of the /

/literature, called α-silicomolybdate. The β-complex is formed when silicic acid reacts with molybdate which has been acidi-:fied with more than about 2 equivalents of acid per gram-ion of $MoO_4^{''}$. Although this compound has the same empirical formula as the α-acid, the structures of the anions are dif-:ferent. The extinction from a given concentration of com-:bined silica is twice as great with the β-acid as with the α-acid. It has also been shown that the β-complex changes spontaneously into the α-acid over a period of several hours. Strickland also concluded that a more fundamental analytical condition is the number of gram-equivalents of hydrogen ions added per gram-ion of $MoO_4^{''}$ and that this should be between 3 and 5 to ensure complete formation of the β-complex; if this exceeds 7 - 10 gram-equivalents per gram-ion, the reaction is impracticably slow.

The following calculation shows that the concen-:trations of molybdate and of acid used in determining silica solubilities during the present work are suitable, and con-:form with the results of Strickland's investigation.

20 ml. of 6N H_2SO_4 contains $\frac{2}{50} \times 6$ gram-ions H^+

$= \underline{0.24 \text{ gram-ions } H^+}$

6 g. $(NH_4)_6\ Mo_7O_{24} \cdot 4H_2O$ contains $\frac{1120}{160} \times \frac{6}{1236}$ gram-ions $MoO_4^{''}$

$= 0.034$ gram-ions $MoO_4^{''}$

100 ml. solution contains $\underline{0.034 \text{ gram-ions } MoO_4^{''}}$.

/These solutions are mixed, thus 120 ml. of solution contains the above equivalents of hydrogen and molybdate ions; 2 ml. is added to the silica solution.

2 ml. of solution contains $\frac{.034}{60}$ gram-ions MoO_4''

$= .00057$ gram-ions MoO_4''

and $.004$ gram-ions H^+

Gram-equivalents of H added per gram-ion of MoO_4''

$= \frac{.004}{.00057}$

$= \underline{7.02}$.

Although this value is slightly higher than that recommended by Strickland, the reaction is not impracticable as can be seen from some of his results quoted in Table 1. For 7 equivalents of acid added per gram-ion of MoO_4'', it is apparent that the half-life of the reacting silica is approx-:imately 2.5 minutes. A yellow-colour development-time of 5 minutes (from the time of addition of acid molybdate) was used throughout this work. According to Strickland, reduction should not, in any case, be delayed for longer than 15 minutes. These results indicate that the method employed ensures com-:plete formation of β - silicomolybdic acid and that the blue colour intensity is given <u>only</u> by this form of the reduced complex. This latter condition is necessary since the α - and β - acids give reduction complexes with different extinc-:tion coefficients. Mixtures of α -silicomolybdous and

TABLE 1. [x]

Variation of $\frac{1}{2}$ life of reacting silica with ratio of gram equivalents of acid added per gram ion of $MoO_4^{''}$.

Equivalent of HCl added to $MoO_4^{''}$.	Approx. $\frac{1}{2}$ life of reacting silica.
6	Very small (pH approx. 0.85)
7	2.5 mins. (pH approx. 0.80)
8	6 mins. (pH approx. 0.75)
9	15 mins.
10	40 mins.
11	3 hours
12	11 hours

(x After Strickland[68])

β -silicomolybdous acids (greenish-blue and royal blue respec-:tively) may be formed if the above conditions do not prevail.

Calibration of colorimeter.

A standard silica solution was prepared by fusing a known weight of finely ground silica (rock crystal) with A.R. sodium carbonate in a platinum crucible, neutralising the excess carbonate with sulphuric acid and diluting to a known volume with distilled water. Various volumes of standard solution were pipetted into Lusteroid tubes containing 25 ml. of borate buffer solution, and the procedure continued as des-:cribed for a normal silica estimation. A graph of colori-:meter reading against silica concentration was plotted, and from this graph concentrations of silica could be obtained, expressed as mg. silica/100 ml. of solution.

/Accuracy of the method.

Eight silica estimations were completed simul-:taneously, using a known constant concentration of silica in solution in each case. This known concentration was such that the intensity of the blue colour was indicated on the most accurate portion of the scale of the EEL absorptio-:meter (30 - 60 units). The deviation of each reading from the mean was used to calculate the percentage arithmetic mean deviation (% A.M.D.). Those sets of readings were obtained at different standard silica concentrations covering the range 30 - 60 units. The mean result was $\pm$ 1.75%.

To maintain this figure, calibration curves were fre-:quently plotted during the course of the work, particularly if cell fatigue was apparent in the instrument, and also on renewal of the cell. By taking such precautions and by using pure reagents, the accuracy of this colorimeter method approaches that of a gravimetric estimation[63].

B. Electron-optical examination of finely ground silica.

Introduction.

During the past few years the solubility theory of silicosis has been widely studied. Gye and Kettle[10] were the first to suggest that the disease is caused by dissolution in the lung fluids of silicic acid derived from inhaled air-:borne dusts, and they induced a necrotic condition in the liver of mice by injection of what they described as colloi-:dal silicic acid. These observations led logically to investigations on the nature of the surface of silica particles. The existence of a high-solubility layer on quartz particles was foreshadowed by the results of Briscoe et al.[69], and of King[21]; Kitto and Patterson[31] observed that the rate of solution of various silicates was greatest in the initial stages, and that the grinding of quartz apparently produces more of the 'highly soluble outer layer.' This interesting concept has been given greater precision by recent work in these laboratories.[54,55,56,57]. The mean thickness of the layer, based on these results and those of Nagelschmidt et al.[58] has been estimated to lie within the limits 0.02 - 0.15μ, and a further estimate, falling within the same limits, is provided by evidence recorded in this work.

If an amorphous layer greater in thickness than 0.02μ exists on finely ground silica particles, it should be possible to detect it by electron-optical methods, particularly

/electron diffraction. X-rays are unsuitable owing to their much greater penetrating power; the electron, because of its mass, is readily absorbed and scattered by matter and cannot penetrate a solid to a depth greater than about 0.1μ, even at an accelerating potential as high as 100kV. Electron diffraction is thus eminently suitable for the investigation of surface layers; removal of the outer disturbed layer would be expected to result in a change in the electron-diffraction pattern produced by the material.

The transmission-type electron microscope is parti-:cularly useful here, since its normal use can be supple-:mented by observing diffraction effects from a selected part of the specimen. It is thus possible to obtain a pattern corresponding to a single particle of quartz, provided that it is small enough to transmit electrons. With larger particles, however, the electron beam can only penetrate regions near the boundary edge; and it is here an advantage to use the 'reflec-:tion' method, in which the electron beam is allowed to fall on a flat compact of the powdered specimen at grazing incid-:ence, so that numerous particles contribute to the diffraction pattern. This technique requires an electron-diffraction camera.

EXPERIMENTAL.

Materials : source and preparation of dusts.

Quartz. - Madagascar quartz crystals, selected for trans-

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/:parency and freedom from occluded impurities, was ground in a jaw-crusher and sieved. The 70 - 90 - mesh fraction was extracted with concentrated hydrochloric acid to remove iron contamination, washed thoroughly with distilled water, dried at 120°, and ground for 17 hours in a mechanical agate mortar.

Lochaline sand. - This material, used by Clelland et al.[54], was of much larger particle size than that required for electron-optical examination. It is a high grade silica mined from the 40-foot Upper Greensand Bed at Lochaline and contains approximately 99.6 - 99.7% silica, 0.2% alumina, with traces of iron oxide, magnesia, vanadia and titania. Successive batches were ground in a mechanical agate mortar for two hours each, and the whole sedimented from distilled water to remove the larger particles. The fine suspended dust was isolated by filtration through two thicknesses of filter paper (Balston No. 1) and dried for three days at 37°.

Fused silica. - The transparent grade of commercial Vitreosil[70] was ground in a Christy-Norris hammer-mill using a ¼-in. screen and sieved to isolate the 70 - 90 - mesh fraction. This was extracted, washed, dried and ground as for quartz.

Removal of the disturbed layer.

Quartz and Vitreosil.- Samples prepared as described above were treated with 40% hydrofluoric acid (A.R.) for five minutes in a polythene beaker. The suspensions were diluted, filtered through two thicknesses of filter paper, washed thoroughly with distilled water, and dried for three days at 37°.

Lochaline sand. - A sample prepared as described above was agitated for 27 days in a thermostat at 37° with borate buffer. The solvent was renewed after isolation of the solid by filtration, and the extraction carried out for a further 29 days. The product was then filtered, washed, and dried as described above.

Solubility of the dusts.

To ensure that the foregoing methods had effectively removed the surface layers, the solubility of each dust in borate buffer was determined before and after treatment. The method used was that described previously and separation of the solid and liquid phases was effected by centrifuging (3450 r.p.m. for 10 minutes) and subsequent filtration through a Ford Sterimat filter pad (Grade SB). The results (Table 11) indicate that the treatments have removed a highly soluble layer from the particle surfaces.

ELECTRON-OPTICAL EXAMINATION OF SAMPLES.

The finely ground silica samples were prepared for electron microscopy by the following two methods :

(i) By shaking up in a glass bottle until a fraction had become airborne, and inverting the bottle over a collodion-covered specimen grid after discarding the undispersed solid.

(ii) By dispersing in pure n-butyl alcohol and spraying from an atomiser on a heated specimen grid.

Both techniques were satisfactory, but (ii) appeared to give a more evenly distributed and representative sample,

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TABLE 11.

Solubility of Quartz, Lochaline sand and Vitreosil in borate buffer (pH 7.5) after 48 hours at 37°; mass/liquid ratio 0.2 g./40 ml.

Sample		mg. / 100 ml.
Quartz :	Untreated	2.30
	Treated	0.15
Lochaline sand :	Untreated	0.99
	Treated	0.44
Vitreosil :	Untreated	6.70
	Treated	1.14

/and was more generally used. Some specimens were shadow-cast by placing them in vacuo (10^{-5} mm.) and evaporating a piece of gold/palladium alloy at 2500° from a tungsten fila-:ment inclined at $\cot^{-1}$ 2.5 to the specimen grid. The metal is deposited over protruding parts of the particles and forms a uniform layer over the collodion film. There is thus no deposition of metal in the geometrical shadows of the particles. A Metropolitan-Vickers EM3 instrument was used in the present work.

Specimens were prepared for the electron-diffraction camera by spraying a dispersion in n-butyl alcohol on a per-:fectly flat and highly polished plate of hard-roller copper. The thickness of the deposit was kept to a minimum in order to avoid charging of the specimen in the electron beam. The dust remained firmly adherent to the copper plate, even though this was held vertically in the camera during examination by the reflection method. A Metrovick electron-diffraction camera was used.

Examination of quartz.

Typical electron-micrographs, taken before and after removal of the disturbed layer, are shown in Figs. 1 and 2. Particle size ranges were calculated by measuring a number of such plates, as follows : before treatment, 0.25 - 10μ ; after treatment, 0.5 - 10μ . The decrease in particle size range after treatment is due to the dissolution of the smaller particles by the hydrofluoric acid, and this treatment has also/

/given the particles a sharper outline (Fig. 2).

Electron-diffraction patterns of these untreated and treated samples (Figs. 3 and 4 respectively) were recorded by the transmission method at an accelerating potential of 60 kV. The background pattern produced by the collodion film consists of very diffuse rings and causes no confusion in interpreting the diffraction patterns. Removal of the layer has resulted in the production of more distinct spots, pointing to a higher degree of crystallinity, in spite of the removal of the smaller and less opaque particles by the hydrofluoric acid treatment. Some degree of crystallinity is, however, apparent from Fig. 3. This is to be expected, since a fair proportion of the 60 - kV. electrons would penetrate an amorphous layer a few hundred Å. units in thickness, to be diffracted on reaching the crystalline core.

The effect of a less penetrating beam was investi-:gated by reducing the accelerating potential to 20 kV. No clear diffraction spots were evident in the pattern produced by the sample with the layer present (Fig. 5), but spots were again observed after removal of the layer, as shown in Fig. 6.

In investigating diffraction patterns by the reflection method at lower voltages, some difficulty was encountered owing to charging of the specimen in the electron beam. Patterns were obtained at 75 kV. only, as shown in Figs. 7 and 8, both of which indicate crystallinity. There are, however,

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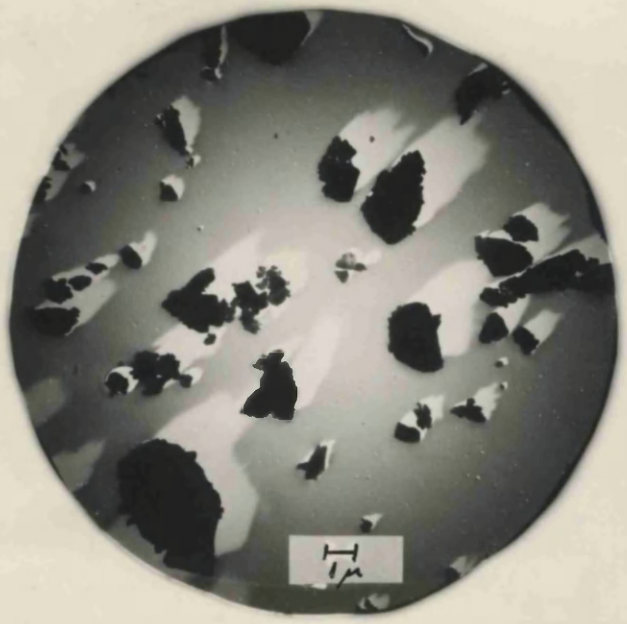

FIG.1. Micrograph of quartz before removal of disturbed layer. Shadow-cast with gold-palladium at $\cot^{-1}$ 2.5 (X3000)

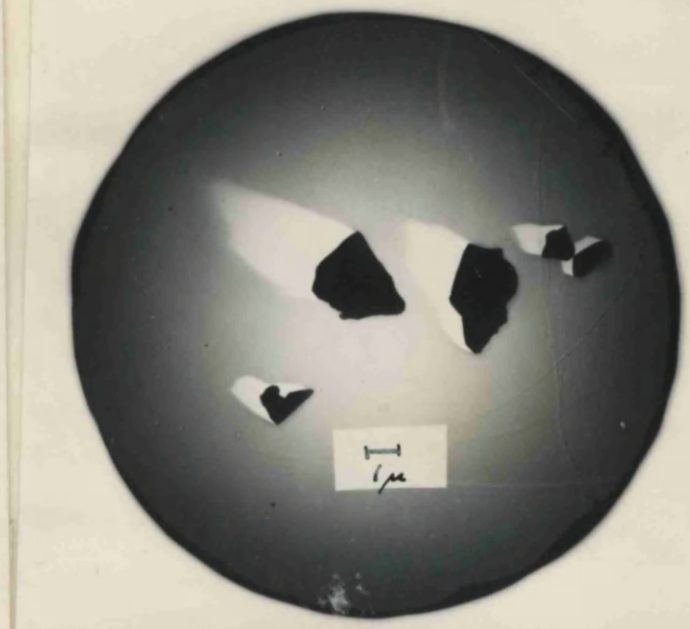

FIG.2. Micrograph of quartz after removal of disturbed layer. Shadow-cast with gold-palladium at $\cot^{-1}$ 2.5 (X 3000)

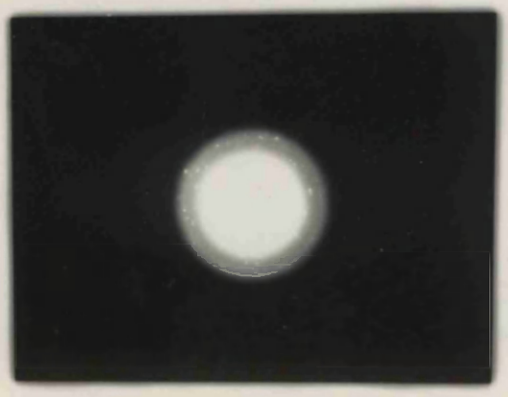

FIG.3. Diffraction pattern of quartz before removal of disturbed layer. Transmission method, with 60-kV. electrons

FIG.4. Diffraction pattern of quartz after removal of disturbed layer. Transmission method, with 60-kV. electrons

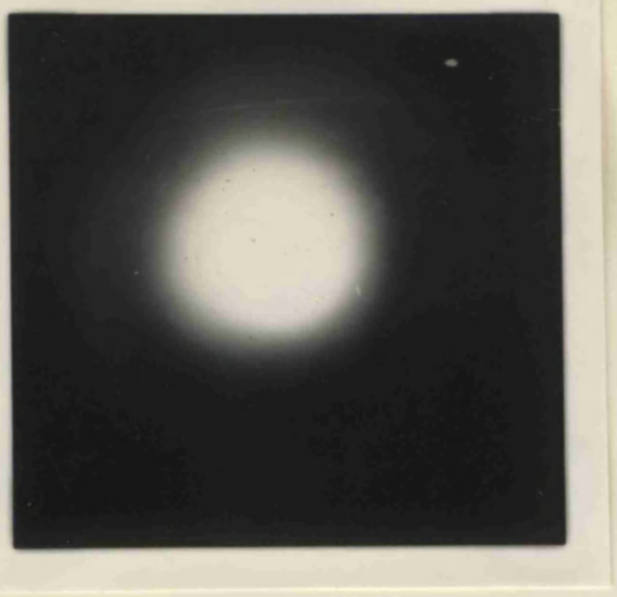

FIG.5. Diffraction pattern of quartz before removal of disturbed layer. Transmission method, with 20-kV. electrons

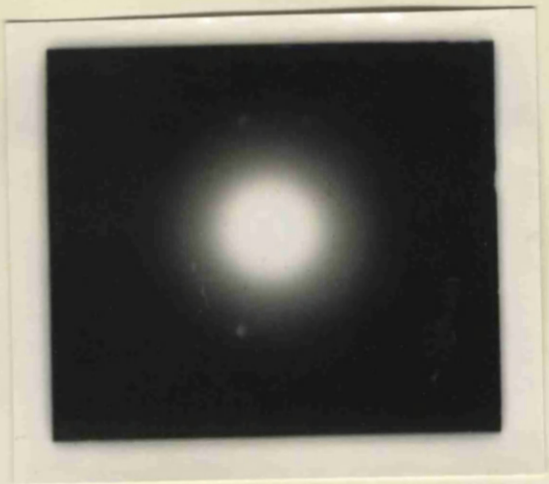

FIG.6. Diffraction pattern of quartz after removal of disturbed layer. Transmission method, with 20-kV. electrons

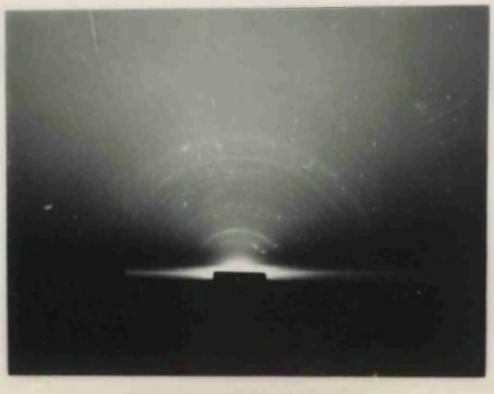

FIG.7. Diffraction pattern of quartz before removal of disturbed layer. Reflection method with 75-kV. electrons

FIG.8. Diffraction pattern of quartz after removal of disturbed layer. Reflection method with 75-kV. electrons

/slight but significant differences. Samples with the layer show a diffraction pattern of rings, with a large number of fine spots superimposed on them. Samples from which the layer has been removed still show the pattern of spots, now less finely dispersed, but the ring pattern has disappeared. There is thus some evidence of a reduction in crystallite size (as distinct from particle size) towards the surface of the quartz grains. The patterns correspond to α-quartz.

Examination of Lochaline sand.

Typical electron-micrographs (Figs. 9 and 10) show that the particle-size ranges of the dusts are : before treatment, 0.25 - 5μ ; after treatment, 0.25 - 5μ . Removal of the disturbed layer by borate buffer has not altered the size range or shape of the particles, in contrast to the effect observed on treating quartz dust with hydrofluoric acid. Micro-diffraction patterns before and after removal of the surface layer are shown in Figs. 11 and 12 respectively, the latter again indicating a higher degree of crystallinity.

Reflection patterns were taken at accelerating potentials of 75 kV. (Figs. 13 and 14) and 25 kV. (Figs. 15 and 16). At 75 kV. both patterns indicate crystallinity, but once again the untreated sample shows a finer dispersion of spots on the diffraction rings, indicating a reduction in crystallite size. At 25 kV. the treated sample still shows a pattern indicating crystallinity but the untreated sample

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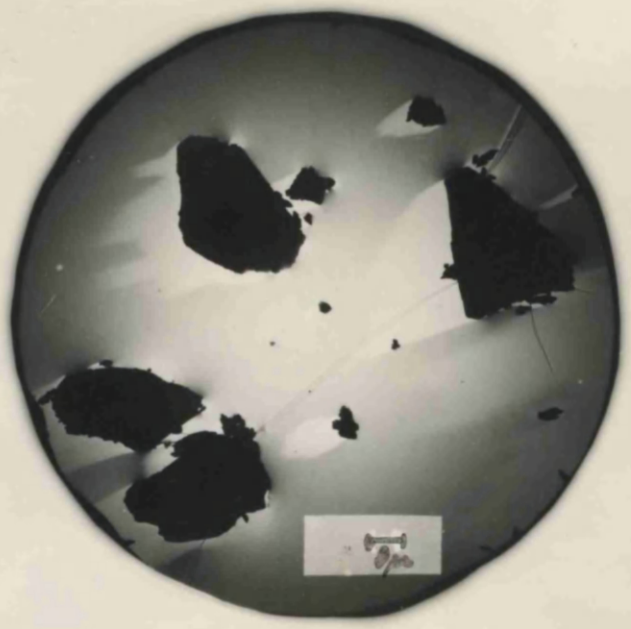

FIG.9. Micrograph of Loch-:aline sand before removal of disturbed layer. Shadow-:cast with gold-palladium at $\cot^{-1}$ 2.5
(X 3000)

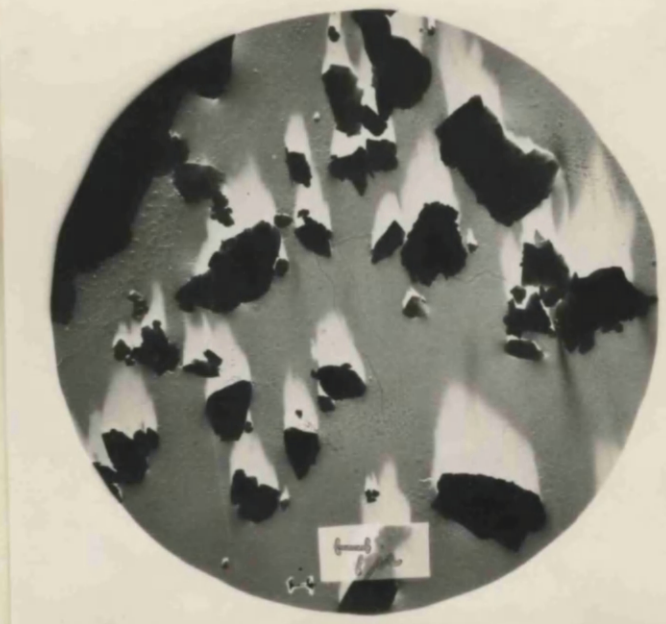

FIG.10. Micrograph of Loch-:aline sand after removal of disturbed layer. Shadow-:cast with gold-palladium at $\cot^{-1}$ 2.5
(X 3000)

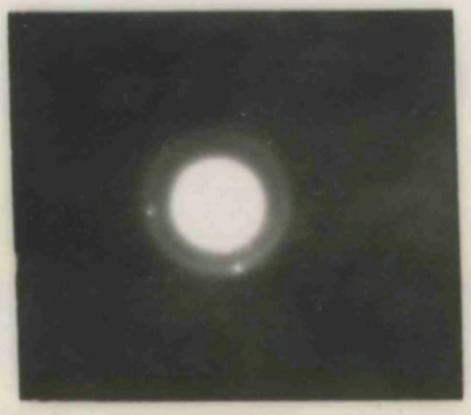

FIG.11. Diffraction pattern of Lochaline sand before removal of disturbed layer. Transmission method, with 60-kV. elect-:rons

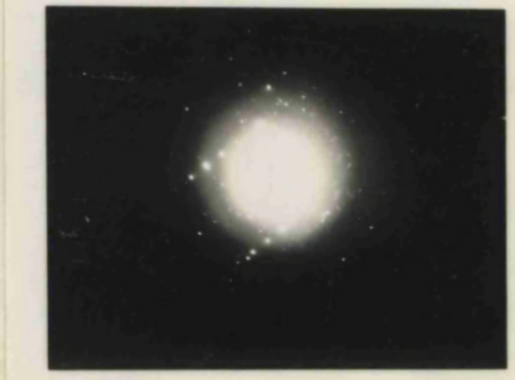

FIG.12. Diffraction pattern of Lochaline sand after removal of disturbed layer. Transmission method, with 60-kV. elect-:rons

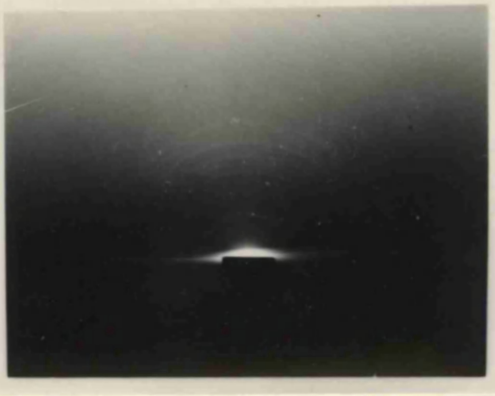

FIG.13. Diffraction pattern of Lochaline sand before removal of disturbed layer. Reflection method, with 75-kV. electrons

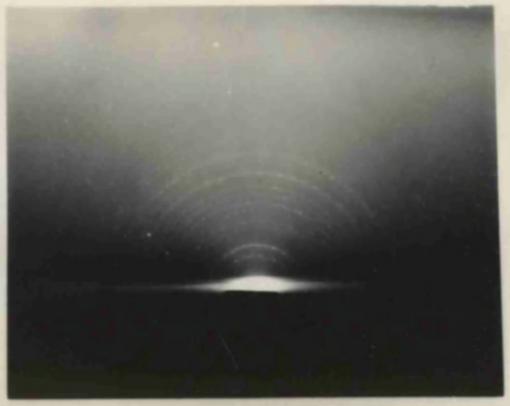

FIG.14. Diffraction pattern of Lochaline sand after removal of disturbed layer. Reflection method, with 75-kV. electrons

FIG.15. Diffraction pattern of Lochaline sand before removal of disturbed layer. Reflection method, with 25-kV. electrons

FIG.16. Diffraction pattern of Lochaline sand after removal of disturbed layer. Reflection method, with 25-kV. electrons

/shows only amorphous halos, and no diffraction rings are present.

Examination of Vitreosil.

Typical electron-micrographs before and after removal of the surface layer (Figs. 17 and 18 respectively) show that the particle size ranges of the dusts are : before treatment, 0.25 - 5μ ; after treatment, 0.50 - 5μ . Here again, as with quartz, acid treatment was found to decrease the particle-size range and define more sharply the outline of the individual particles. If, as is normally assumed, the material is wholly amorphous, removal of the layer should pro-:duce no change in the diffraction pattern; this was found to be so. The patterns obtained by the transmission method showed only collodion bands, and indicated no crystallinity; a typical diffraction pattern is shown in Fig. 19.

This result was confirmed by the reflection method at 75 kV. Fig. 20 is a typical record and shows amorphous halos with no evidence of crystallinity, resembling those obtained for untreated Lochaline sand at an accelerating poten-:tial of 25 kV. (Fig. 15).

Discussion.

Existence of an amorphous surface layer.

The foregoing results provide strong confirmatory evidence for the existence of the previously postulated amor-:phous layer. To establish the presence of such a layer by

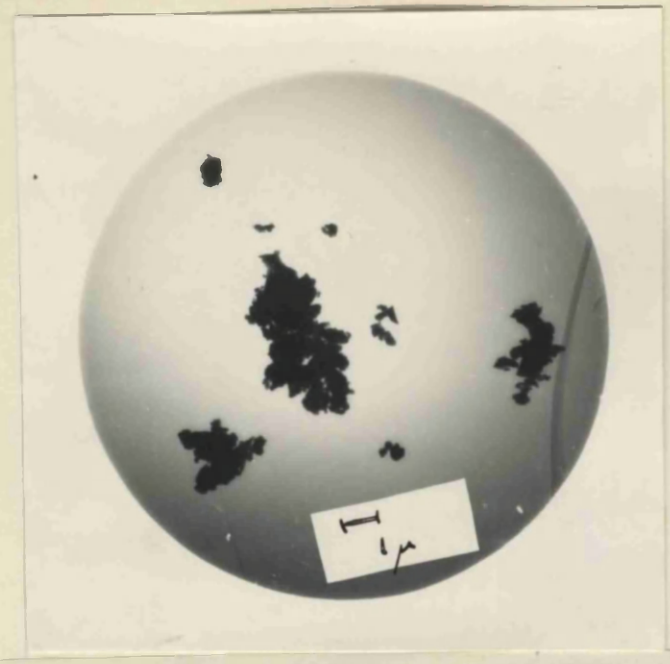

FIG.17. Micrograph of Vit-:reosil before removal of disturbed layer (X 3000)

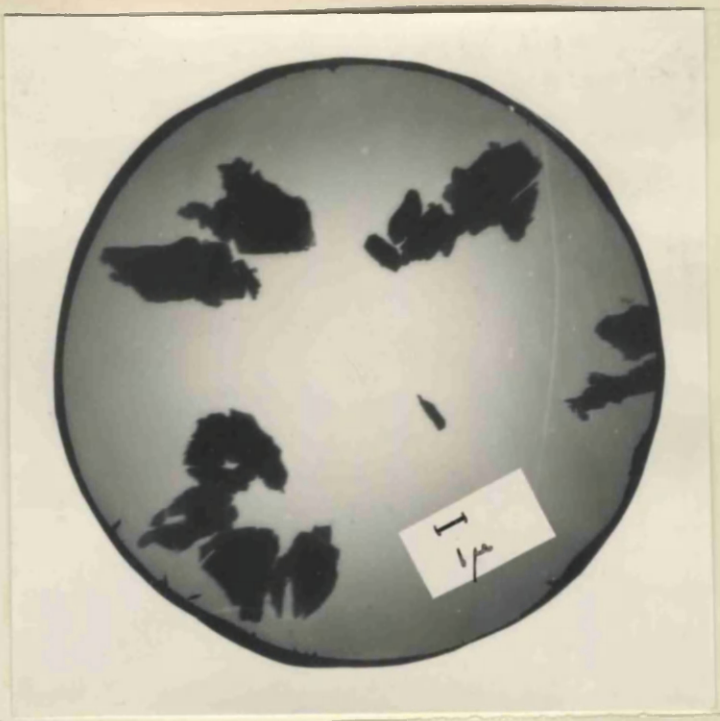

FIG.18. Micrograph of Vit-:reosil after removal of disturbed layer (X 3000)

FIG.19. Diffraction pattern of Vitreosil, before and after re-:moval of disturbed layer. Transmission method, with 60-kV. electrons

FIG.20. Diffraction pattern of Vitreosil, before and after re-:moval of disturbed layer. Reflection method, with 75-kV. electrons

/means of electron diffraction is much more difficult for finely divided material than for larger crystals, but even on the basis of the powder photographs (particularly at 25 kV), a distinction is apparent between the patterns produced by particles with and without the original surface layer. Although still significant, this distinction is less obvious at higher accelerating potentials.

Mean thickness of surface layer.

The presence of the amorphous surface layer having been established, a rough estimate of its mean thickness can be made. Cochrane[71] has shown that the diffraction pattern of a single crystal of copper is completely obliterated when nickel is deposited on the surface to a thickness of 400 Å; Thomson and Cochrane[72] have estimated that in general 30-kV. electrons can penetrate a solid to a depth of about 400 Å. On the other hand, silica films 100 Å. in thickness (Prepared by evaporating silica in a high vacuum) are used in electron microscopy as specimen-supporting films[73], and are fairly transparent to 25-kV. electrons. A film three or four times this thickness, however, will not be penetrable by such a beam.

For 25-kV. electrons it can be estimated that a thickness of about 300 Å. of silica will obscure the effects of the crystalline core. Quite apart from decrease in trans-:parency, a layer thicker than this would impart incoherence to the beam, rendering regular diffraction impossible. It is thus possible to place a lower limit of about 300 Å. (0.03 μ)

/to the layer-thickness. On the other hand, since 75-kV. electrons are able to penetrate the surface layer on quartz and Lochaline-sand dusts and reveal the underlying crystal-:linity, the upper limit of layer-thickness appears to be about 600 Å. (0.06μ). Table 111 summarises estimates of mean layer-thickness made on the basis of several widely different types of physical and chemical measurements; although the numerical results show some scatter, the general agreement is good, the bulk of the evidence favouring a mean thickness of approximately 0.03μ. Indeed, better agree-:ment would be surprising, since the various measured quan-:tities on which the calculations are based are a reflection of quite different properties, which may follow different distribution gradients across the total disturbed zone, inwards from the surface towards the crystalline core. Furthermore, the calculations are based upon and rendered possible by a number of arbitrary assumptions and simplifications. For example, the assumption of uniform particle size, spherical particles, and a sharply-defined discrete surface layer is certainly an over-simplification; in any case, the various authors quoted have not all used the same method of measuring particle size. In spite of all these limitations upon accuracy, a surprisingly consistent picture emerges, and it is doubtful whether the 'thickness' of a layer that is not completely homogeneous and discrete can at this stage be given

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TABLE 111.

Estimated mean thickness of disturbed layer of quartz.

Basis of calculation.	Approx. thickness.
Solubility measurements	0.02 - 0. 03*
Solubility measurements	0.03†
X-ray diffraction	0.03
Density measurements	0.03 - 0.05
Electron diffraction (present work)	0.03 - 0.06
Durkan's correction factor	0.04 - 0.07‡
Differential thermal analysis	0.11 - 0.15

*Calculated from data by Clelland et al.[54]

† " " " " King.[21]

‡ " " " " Durkan.[74]

/a more precise meaning.

Existence of an intermediate transitional layer.

There are further small but significant differences between the patterns obtained from samples with and without the disturbed layer at 75 kV. With quartz, ring patterns are observed for the untreated sample, whereas for the treated sample only rings of spots are obtained (cf. Figs. 7 and 8). The crystallites responsible for such ring patterns must be very much smaller than the order of size in the original sample (about 1μ). It appears that surface layers of these crystals may be broken up into a fine state during the grinding process, the crystallite size decreasing outwards from the core to the truly amorphous surface layer.

No such difference is apparent in the corresponding patterns from Lochaline-sand dusts (Figs. 13 and 14). Here the spots are more distinct in the pattern from the treated sample, but both treated and untreated materials show a ring pattern. It is clear, however, from the electron-micrographs that removal of the surface layer by borate buffer treatment did not proceed to the extent of detaching the minute broken-up crystallites from the core. Treatment of the quartz dust by hydrofluoric acid, on the other hand, removes both the outer amorphous layer and the underlying intermediate layer of crystal-:lite fragments.

Conclusion.

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/Conclusion.

The foregoing results strongly confirm the pre-:viously expressed view that 'there exists on powdered quartz-particles a vitreous skin, produced by surface flow during grinding and blending via a transitional layer into the truly crystalline core.'

PART II.

A. THE EFFECT OF ACIDS ON THE SOLUTION PROPERTIES OF SILICIOUS DUSTS.

B. SOME SORPTION PROPERTIES OF SILICIOUS DUSTS.

A. The Effect of Acids on the Solution Properties of Silicious Dusts.

Introduction.

The foregoing results have given greater precision to the 'disturbed surface-layer' concept investigated by other workers in this field. It was suggested that the high solu-:bility of silica particles bearing this disturbed layer was due to the superior solubility of amorphous silica, though it is possible that the presence of very minute shattered particles, adhering to the outer skin (as shown by the electron-micro-:graphs in Part 1 (B)), is at least a contributory factor.

Clelland et al.[54] showed, in addition, that treat-:ment of a pure rock crystal dust with mineral acid produces a decrease in silica-solubility, whereas an increase was observed for a naturally occurring Lochaline-sand dust, which contains small amounts of impurities, mainly alumina. This increase was thought to correspond to the development of a modified surface-layer on the Lochaline-sand particles, though not necessary one identical with the disturbed layer produced by crushing and grinding operations.

When the amorphous surface layers of these quartz and Lochaline-sand dusts were removed by treatment with a borate buffer during extractive solubility experiments, subsequent treatment with mineral acid produced no change in the solu-:bility of the quartz dust, but again markedly increased that

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/of the Lochaline sand. This enhanced solution-rate of Lochaline sand was reduced to the pre-treatment value by a subsequent solution period of approximately three days, whereas originally it required a period of 20 days to reduce the high rate of solution due to the presence of the disturbed layer of amorphous silica.

Because of these properties of an impure silicious dust and also because pure rock crystal reacts with mineral acid in a different manner, it is not unreasonable to con-:clude that the modified surface-layer produced on Lochaline-sand particles by mineral acid differs from the disturbed layer produced by crushing and grinding.

It is thus evident that when a silicious material has been purified by treatment with acid, the results of sub-:sequent solubility experiments must be cautiously interpreted. For example, King[27] found that the solubility of sericite, when compared with that of other silicious minerals (e.g., kaolin, biotite), was very high and close to that of pure quartz. King recalled, however, that the material had been treated with hydrochloric acid during preparation; and he con-:cluded that the effect might have been caused by a change in the lattice structure of the outer layers of the sericite, enabling silica to pass more readily into the solvent medium. Emmons and Wilcox[75] also reported high dissolution figures for sericite; but, once again, their silicate dusts were treated with hydrochloric acid during purification. Similar results

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/were obtained by Francis (unpublished observation)[76] for asbestos fibres. He pointed out that the metallic elements may be dissolved in the acid medium leaving behind a silicious residue. A result which strongly supports the solubility theory of silicosis is to be found in further investigations by King[77]. He showed that, while sericite exposed to water and neutral salt solutions caused very little fibrosis in the lungs of animals, a sample of the same material after extrac-:tion with dilute hydrochloric acid was markedly pathogenic. This striking contrast can be observed in King's published photographs of the corresponding lung sections. The solu-:bility of this sericite sample was also considerably increased.

The same caution is obviously necessary in inter-:preting pathogenicity experiments. For example, Rüttner[78] made the interesting observation that a silica dust extracted from the lungs of deceased silicotics is as pathogenic as a freshly formed dust; but the significance of this is again to some extent obscured by the fact that extraction of the dust from the lung tissues entailed treatment with strong acid.

The present work was designed to elucidate the nature of the change undergone by the surface of silicious dust particles on extraction with mineral acid.

EXPERIMENTAL. /

/EXPERIMENTAL.

Materials : Source and preparation of dusts.

Lochaline-sand dusts are referred to by the letters LAS followed by a batch number. Particle sizes were measured microscopically, using a calibrated graticule. For some samples, limits of particle size are given, and the average particle size is calculated as $(\Sigma d)/n$, where d = diameter of particle and n = number of particles. For each of the fol-:lowing materials, n was approximately 400.

(i) Lochaline-sand dust (LAS5) was prepared from the natural sand, as described elsewhere[54], by repeated sedimentation from distilled water to remove all particles below 125μ, and dried at 120°.

(ii) Rock-crystal dust (150 - 500μ : $(\Sigma d)/n$ = 237μ) was prepared from Madagascar quartz crystals, specially selected for purity and ground in an agate mortar. The dust was sedi-:mented from distilled water to remove fine material and dried at 120°.

(iii) Olivine (40 - 420μ : $(\Sigma d)/n$ = 140μ) and (iv) Ortho-:clase (55 - 354μ : $(\Sigma d)/n$ = 135μ) dusts were prepared by grinding the respective minerals (both from Arendal, Norway) in an agate mortar, and sized by sieving and sedimentation from water.

(v) Sandstone dust (180 - 455μ : $(\Sigma d)/n$ = 300μ) was pro-:duced from a sandstone from Locharbriggs, Dumfries (97.8%

/

/SiO_2 by evaporation with hydrofluoric acid, by grinding in an agate mortar. The sieved 50-70- mesh fraction was sedi-:mented from water to remove fine dust.

(vi) DRC silica dust is produced commercially by grinding a high-silica rock from North Wales. It contains about 7% of impurities and has an average particle diameter of 1μ.

Effect of acid extraction on the solubilities of some silicious dusts.

Table 1V summarises the effect of acid extraction on the solubilities of dusts containing both free and com-:bined silica. (The last column of Table 1V will be referred to in a later section). All dusts extracted, except rock crystal, show increased solution-rates. The results are not comparable with each other on a rigorously quantitative basis, since particle sizes vary, and since arbitrary mass/liquid ratios were chosen for convenience in determining solubilities. The indicate, however, the general behaviour of each material on treatment with hydrochloric acid.

Great care was taken to exclude all impurities from the rock crystal sample during preparation. It has been shown that Lochaline sand is more soluble in acid solutions than in solutions of pH 7.5, while quartz is less soluble[79]. DRC and Lochaline-sand dusts contain appreciable amounts of alumina, whereas rock crystal contains no alumina. Alumina, being an amphoteric oxide, is more soluble in acidic or alka-:line solutions than in solutions of pH 7.5. Since alumina

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TABLE IV.

Effect of acid extraction on the solubilities of some silicious dusts.

Solubilities are expressed as mg./100 ml. after 48 hours in borate buffer (pH 7.5) at 37°, pre-treatment period 48 hours with N hydrochloric acid.

Sample.	Mass/liquid ratio for pretreat-:ment.	Mass/liquid ratio for solubility.	Solubility before extraction	Solubility after extraction	Solubility after extraction and heating.
Ortho-clase	4g./40ml.	1g./40ml.	0.05	0.26	0.10
Sand-stone	10g./40ml.	4g./40ml.	0.58	0.65	0.55
Rock crystal	5g./40ml.	4g./40ml.	0.43	0.24	-
DRC silica	2g./40ml.	0.4g./40ml.	0.86	6.00	1.04
LAS 5	10g./40ml.	4g./40ml.	0.31	1.71	1.02
Olivine	5g./40ml.	0.6g./40ml.	0.07	3.80	0.60

/depresses the solubility of silica, its removal at low pH values would account for the enhanced solubilities of the impure dusts shown in Table lV. Since the rock crystal contained no significant impurities, the reduction in solu-:tion-rate might be attributed to the dissolution of a por-:tion of the highly-soluble disturbed surface layer. This conclusion is supported by the observation of Clelland et al.[54] that acid treatment does not change the solution-rate of a quartz dust from which the disturbed layer has been removed by a borate buffer. It was also concluded by Heavens[80], as a result of an electron-optical study of a quartz surface, that treatment with concentrated hydrochloric acid removes a strained, but still crystalline, surface layer.

Removal of alumina during acid extraction.

Denny, Robson, and Irwin[23] have shown that the addition of activated alumina (30 mg.) to quartz (lg.) reduces the solubility of the quartz by as much as 89%. It is, there-:fore, not unreasonable to predict that the removal of ca. 0.2% of alumina from a sample of Lochaline sand by acid treatment would increase the solubility measurably.

To demonstrate the removal of alumina, the staining procedure introduced by Denny et al.[23] was adopted. Pure Madagascar quartz pebbles were placed in contact with dis-:tilled water in six stoppered bottles containing the various dusts detailed in Table V. The bottled samples were allowed to stand, with occasional shaking, for 70 days; the pebbles

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TABLE V.

Removal of alumina from LAS 5 and DRC by acid extraction.

(Demonstrated by method of Denny, Robson, and Irwin[23])

Dust used.	Final colour of quartz-pebble surfaces.
LAS 5(X)	Colourless (= no alumina monohydrate on surface)
DRC (X)	" (= " " ")
LAS 5	Pink (= a little alumina monohydrate on surface)
DRC	" (= " " ")
Ground alumina	Red (= much alumina monohydrate on surface)
Aluminium filings	" (= " " ")

(X = previously extracted with concentrated hydrochloric acid)

/were then removed, cleaned with distilled water, placed in a 1% solution of aurine tricarboxylic acid (buffered at pH 4.0), heated for 3 minutes at 70°, and finally washed and dried. Table V shows clearly that alumina had been removed from LAS 5 and DRC during acid extraction; and, as will be seen later, this process can only contribute to the increase in solubility of the impure dusts.

Effect of heat-treatment on solubility of acid-extracted silica dusts.

As already pointed out, it is unlikely that the highly soluble modified layer generated on Lochaline sand and DRC silica particles by mineral acids is similar in nature to the disturbed layer of amorphous silica produced by grinding. It was, however, thought likely that if the acid-modified surfaces also consist of amorphous silica the solubility of a sample of acid-extracted Lochaline sand might be reduced by heating the dust above 1000°, for it has been suggested that fused silica may undergo a structural change at such tempera-:tures,[81], producing the symmetrical and stable lattice chara-:cteristic of crystalline (devitrified) silica. Some such change has been observed, though at temperatures as low as 750°, within the surface layer of membranes of wholly amor-:phous silica[53]. To investigate the matter, the effect of heat on the enhanced solution-rate of acid-extracted LAS 5 has been studied as follows.

LAS 5(C) was prepared by extracting the natural sand with concentrated hydrochloric acid for 22 hours, washing thoroughly, and drying at 120°. LAS 5(A) was prepared simi-:larly by extracting for 4 hours with concentrated hydro-:chloric acid. Samples were weighed into a combustion boat of glazed transparent Vitreosil, and heated in a combustion tube of the same material inserted in an electric furnace, the temperature of which was thermostatically controlled and measured by a chromel-alumel thermocouple.

In a preliminary experiment, LAS 5(C) was heated for 44 hours at 1150° under the above conditions; this was repeated using LAS 5(A), and extractive solubility results were obtained for each dust. Table Vl shows that high-temperature treatment has reduced the solubilities of both these dusts, of different initial solubilities; and it was also found that heating for only 5 minutes at this temperature is sufficient to reduce the solubility of LAS 5(C) to its original value.

The threshold temperature at which the solution-rate of LAS 5(C) begins to decrease was found by heating 4g. samples for 30 minutes at various temperatures, solubilities being determined after 48 hours in borate buffer (pH 7.5) at 37° (mass/liquid ratio 4g./40 ml.). The results are shown in Fig. 21, where A and B are datum lines representing the original solubilities of LAS 5(C) and LAS 5 respectively. It is very unlikely that the observed effect is due to recrystal-:lisation of amorphous material on the surface of the particles;

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TABLE V1.

Effect of heat-treatment on the solubility of acid-extracted Lochaline-sand dusts.

Extractive solubilities in borate buffer (pH 7.5) at 37°: mass/liquid ratio, 4g./40 ml.

Solution period (hours)	LAS 5 mg./100 ml.	LAS 5(C) mg./100 ml.	LAS 5(C) after heating mg./100ml.	LAS 5(A) mg./100ml.	LAS 5(A) after heati mg./100 ml.
24	0.24	1.41	0.24	0.30	0.22
24	0.17	0.37	0.18	0.20	0.16
72	0.34	0.45	0.36	0.32	0.35
72	0.21	0.22	0.24	0.23	0.21

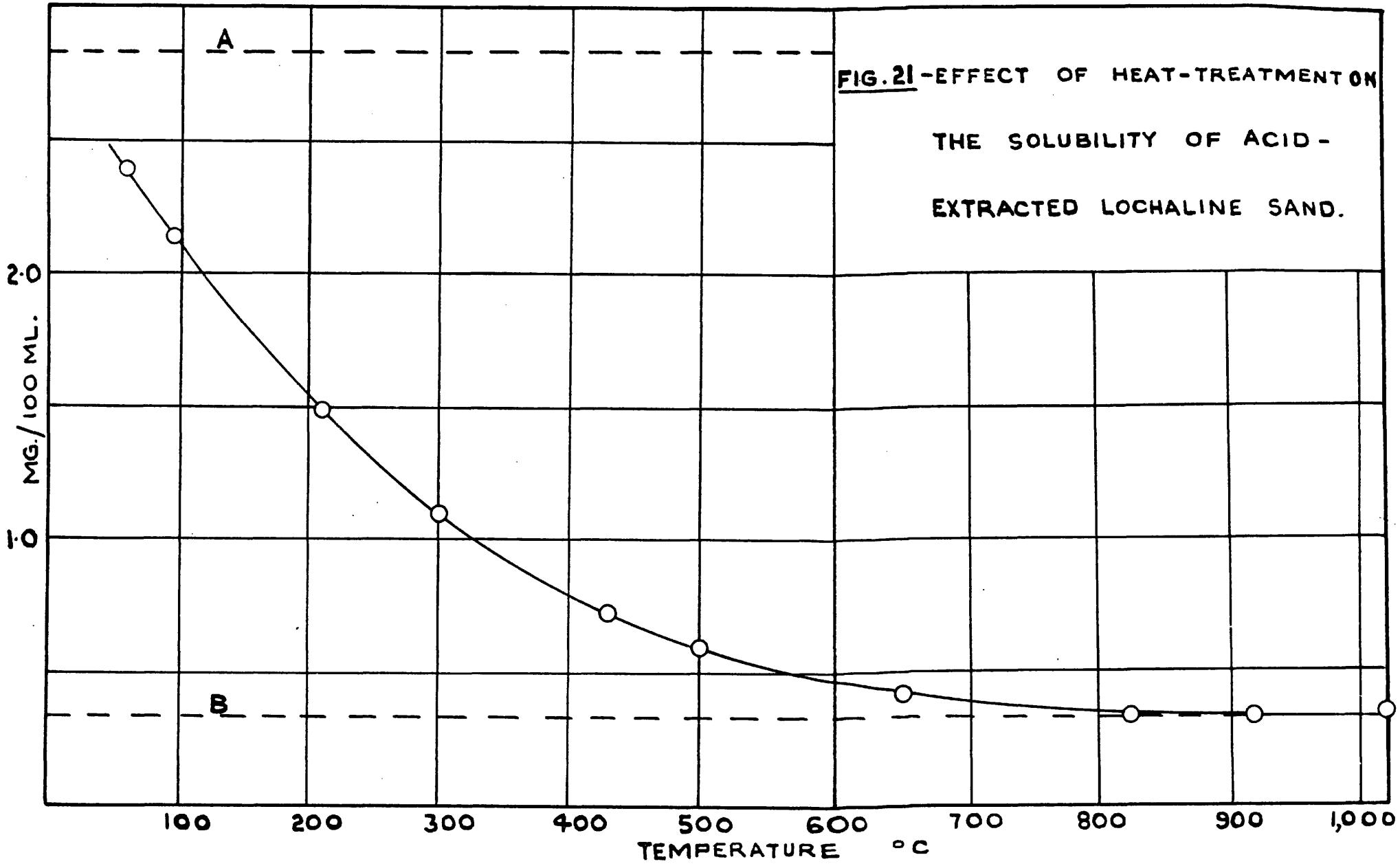

FIG. 21 - EFFECT OF HEAT-TREATMENT ON THE SOLUBILITY OF ACID-EXTRACTED LOCHALINE SAND.

/for this process would be expected to require temperatures greater than 1000°, whereas a distinct reduction in solubility is observed even after 30 minutes at only 60°. Furthermore, it has been found that heating 4g. samples of LAS 5 for 30 minutes over the range of temperatures shown in Fig. 21 does not markedly change the solubility (Table V11).

Similar results have been obtained with DRC silica. A sample was dried in a vacuum oven for 4 hours, extracted for 20 minutes with boiling concentrated hydrochloric acid, fil-:tered after addition of distilled water, washed thoroughly to remove acid and dried at 37°. 0.5g. samples were heated for 30 minutes at various temperatures; their resultant solu-:bilities are plotted in Fig. 22 (lower curve) as mg./100 ml. after 48 hours in borate buffer (pH 7.5) at 37° (Mass/liquid ratio 0.4g/40 ml). A and B are datum lines representing the solubilities of the acid-treated and untreated dusts respec-:tively; the experimental curve tends to approach the latter.

At the comparatively low temperature of 500°, the reduction in solubility is large; and this can hardly be due to devitrification of a disturbed surface-layer. This solu-:bility/temperature effect is common to all the silicious dusts tested, as shown by the last column of Table 1V, obtained by estimating the solubilities of each acid-treated dust after heating at 775° for 30 minutes. If the increased solution-rates of these impure silicious dusts, LAS 5 and DRC silica/

TABLE V11.

Effect of heat-treatment on the solubility of natural Lochaline sand.

Solubilities of LAS 5 in borate buffer (pH 7.5) after 24 hours at 37°; mass/liquid ratio, 4g./40 ml.

Temperature of heat-treatment	mg./100 ml.
Untreated	0.22
190°	0.21
385°	0.23
685°	0.25
900°	0.23
1000°	0.23

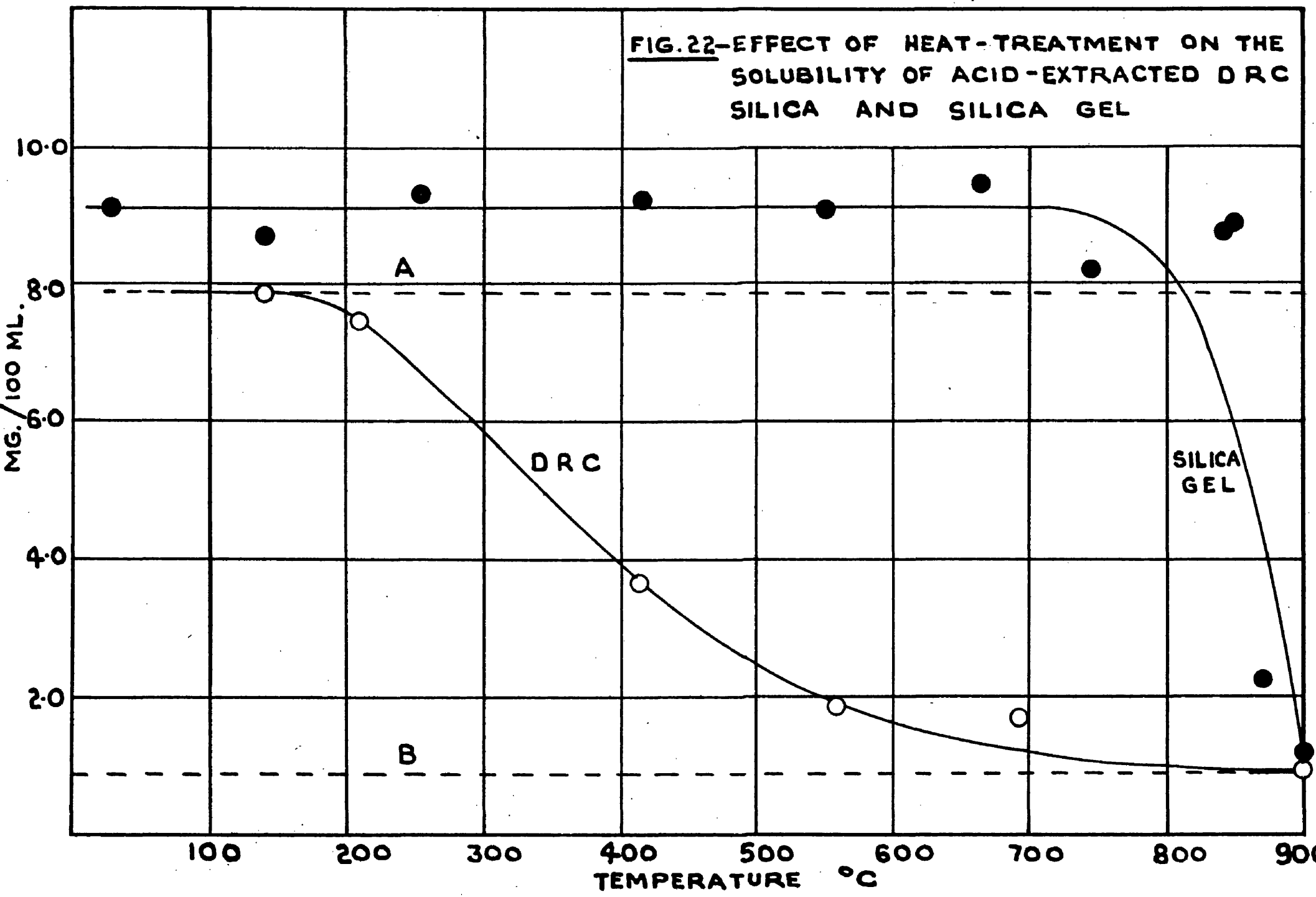
FIG. 22—EFFECT OF HEAT-TREATMENT ON THE SOLUBILITY OF ACID-EXTRACTED DRC SILICA AND SILICA GEL
10·0
8·0
6·0
4·0
2·0
MG./100 ML.
A
B
DRC
SILICA GEL
100
200
300
400
500
600
700
800
900
TEMPERATURE °C

/in particular, were due only to the removal of alumina, it is unlikely that such a solubility/temperature effect would occur at all; and two other possible contributing causes will now be considered - the formation of a hydrated surface layer, and of a layer of adsorbed hydrogen ions.

Formation of a hydrated surface layer.

One obvious possibility for consideration is that hydration of the surface layers of silica particles may occur during acid treatment, with resultant formation of silicic acid in the solvent. Silica gel possesses such a surface, owing to the retention of water molecules by negative hydroxyl groups and formation of hydrogen bonds[82], giving rise to hydro-:nium ions (H_3O^+). If this hydrated layer is similar to the layer imparting a high solution-rate to acid-treated Lochaline sand and DRC silica particles, silica gel should show a similar solubility/temperature effect.

Samples of a commercial silica gel were therefore heated for 30 minutes at various temperatures; and the change in solubility over the range 30 - 900° is shown in Fig. 22 (upper curve), the results being expressed as mg./100 ml. after 24 hours in borate buffer (pH 7.5) at 37° (mass/liquid ratio 4g./40 ml.). The solubility begins to decrease at 700°, while for LAS 5(C) and DRC silica an almost immediate reduction was observed. At 700°, a visible change occurred in the gel particles, which gradually became opaque; and this change was /

/fully established at 900°. The results of Weyl[82] suggest that this effect is due to instability of the hydronium ions at high temperatures, with consequent formation of anhydrous silica, the solubility of which is much lower than that of the gel.

Such an effect is not observed, however, with the acid-treated dusts, reduction in solubility occurring here at low temperatures. The nature of the gel surface is thus apparently quite different from that of the acid-extracted materials.

Since increase in solution-rate might be connected with adsorption of atmospheric moisture on the particle sur-:faces, the effect of very high vacuum on the solubilities of acid-treated silicious dusts was investigated. Such treatment might be expected to remove adsorbed moisture.

Samples of LAS 5(C) and acid-treated DRC silica were maintained in a high vacuum (10^{-5} mm.) for about 2 hours; solu-:bilities were determined before and immediately after treatment. No change was apparent (Table Vlll) in the solubilities of the dusts; and, in conjunction with the foregoing results, this suggests that the dusts do not show enhanced solution-rates by virtue of hydrated silica surfaces.

Formation of a layer of adsorbed hydrogen ions.

An alternative possibility is the adsorption of hydrogen ions on the surface irregularities formed by removal of impurities during acid extraction of LAS 5 and DRC silica. The presence of these positive ions during solubility deter-

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TABLE VIII.

Effect of pre-treatment in high vacuum on the solubilities of acid-extracted Lochaline sand and DRC silica.

Solubilities are expressed as mg./100 ml. after 48 hours in borate buffer (pH 7.5); mass/liquid ratio 4g./40 ml. (LAS) and 0.4 g./40 ml. (DRC).

Sample.	mg./100 ml.
LAS 5(C)	1.24
LAS 5(C) *	1.25
LAS 5	0.35
DRC (acid-extracted)	9.00
DRC (acid-extracted) *	8.90
DRC	1.05

(* - vacuum-treated sample)

/:minations may increase the concentration of silicic acid by attracting a greater number of hydroxyl groups from the solvent medium to the surface of the particles. On this basis, solu-:bility should be dependent on the pH of the extraction solution, a view confirmed by the following experiments.

4g. samples of LAS 5 were extracted for 48 hours at 37° with 40 ml. of hydrochloric, sulphuric, and nitric acids of varying pH. The solubilities were determined after 48 hours in borate buffer (pH 7.5) at 37° (mass/liquid ratio 4g./40 ml.). The results are shown in Fig. 23, where the datum line A represents the solubility of the untreated dust (LAS 5) under the above conditions. For each acid, the effect is greatest at the lowest pH, where the concentration of hydrogen ions is very high. At pH values near neutrality the effect is not apparent, the datum line A lying wholly above each curve. At pH 4.5 alumina becomes decreasingly soluble in the extrac-:tion medium, and hydrogen-ion adsorption will be less marked than at lower pH values. The effect of the solvent is to reduce the solubility of the dust, whereas a surface layer of adsorbed hydrogen ions will tend to increase it; hence, at higher pH values, the former effect will predominate, depres-:sing the solubility below the datum line.

Table 1X supports this idea. 4g. samples of LAS 5 were extracted for 48 hours at 37° with 40 ml. of sulphuric acid of varying pH. The pH of each solution showed an increase

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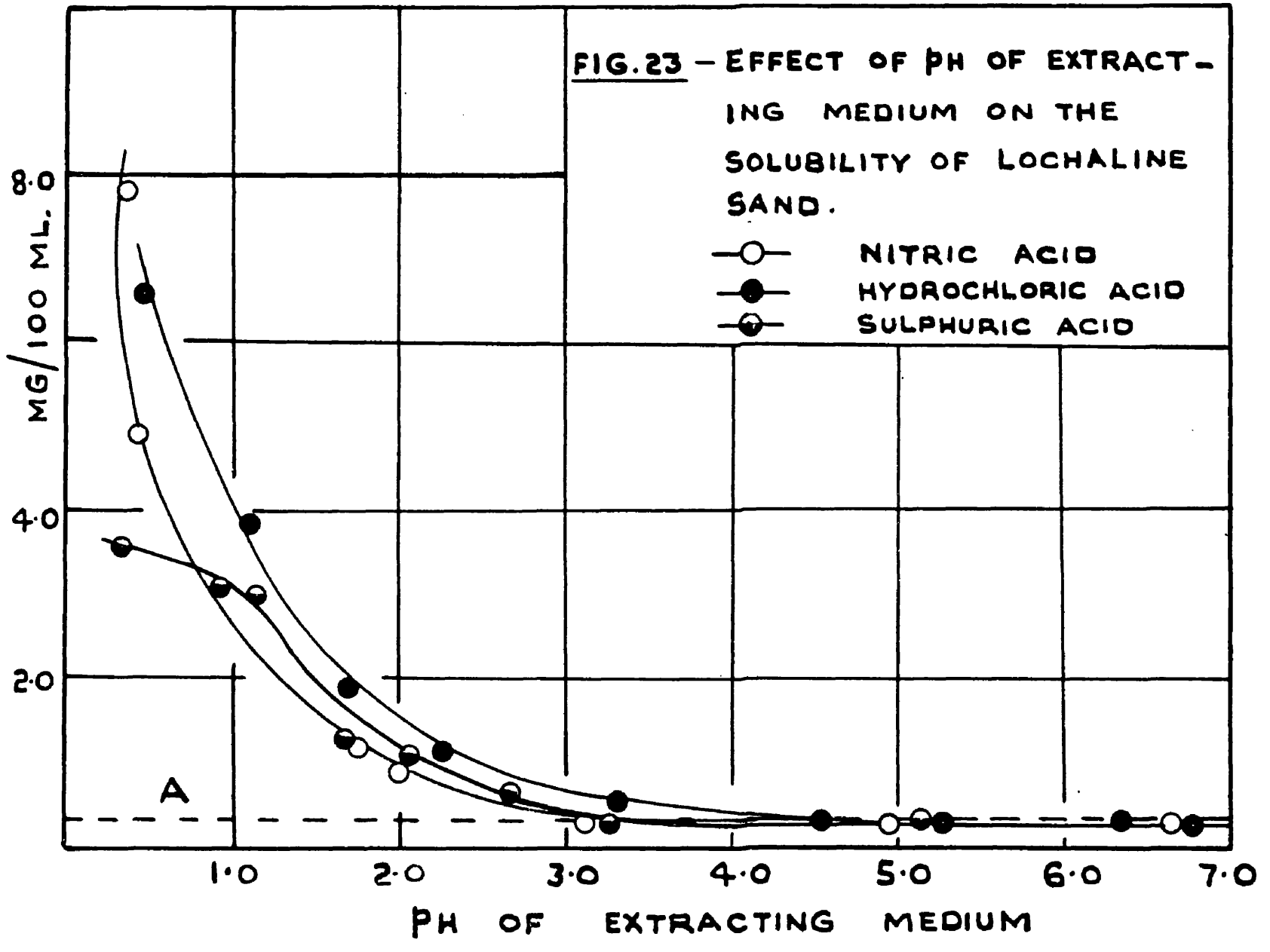
FIG. 23 – EFFECT OF PH OF EXTRACTING MEDIUM ON THE SOLUBILITY OF LOCHALINE SAND.
NITRIC ACID
HYDROCHLORIC ACID
SULPHURIC ACID
MG/100 ML.
8·0
4·0
2·0
A
1·0
2·0
3·0
4·0
5·0
6·0
7·0
PH OF EXTRACTING MEDIUM

TABLE IX.

Variation in pH of extracting medium

(sulphuric acid)

pH before extraction	pH after extraction
2.1	2.2
3.2	3.6
3.6	5.1
4.1	6.7
4.8	6.7
5.4	6.7
6.2	6.6

/after the extraction; and this decrease in concentration of hydrogen ions may possibly be accounted for by their adsorp-:tion on the particle surfaces.

It would thus seem that hydrogen ions are adsorbed on the surfaces of the dust particles during acid treatment. Reduction of this enhanced solution-rate would be expected to occur during pre-treatment with solvents of increasing pH. The following considerations further clarify this concept. Results obtained by Clelland et al.[54] on the change in solu-:bility of acid-extracted Lochaline sand with variation in pH of a pre-treatment solution are shown in Fig. 24. (LAS 5(A) was prepared by treating a quantity of LAS 5 for 4 hours with cold concentrated hydrochloric acid, and LAS 5(B) by treating LAS 5 for 1 hour with hot and 20 hours with cold concentrated hydrochloric acid).

It can be seen that acidic buffer solutions ($pH < 4$) increase the solubility of LAS 5, a result similar to that shown in Fig. 23. With LAS 5(A), however, solutions of $pH < 4.75$ are capable of raising the solubility of the dust above the corresponding datum line. At higher pH, neutra-:lisation of adsorbed ions may occur; and as the pH increases, silicic acid becomes more soluble in the pre-treatment buffer and the dust less soluble in borate buffer. A similar effect is shown by dust LAS 5(B); here, however, solutions of lowest pH do not increase the solubility, but merely dissolve a portion

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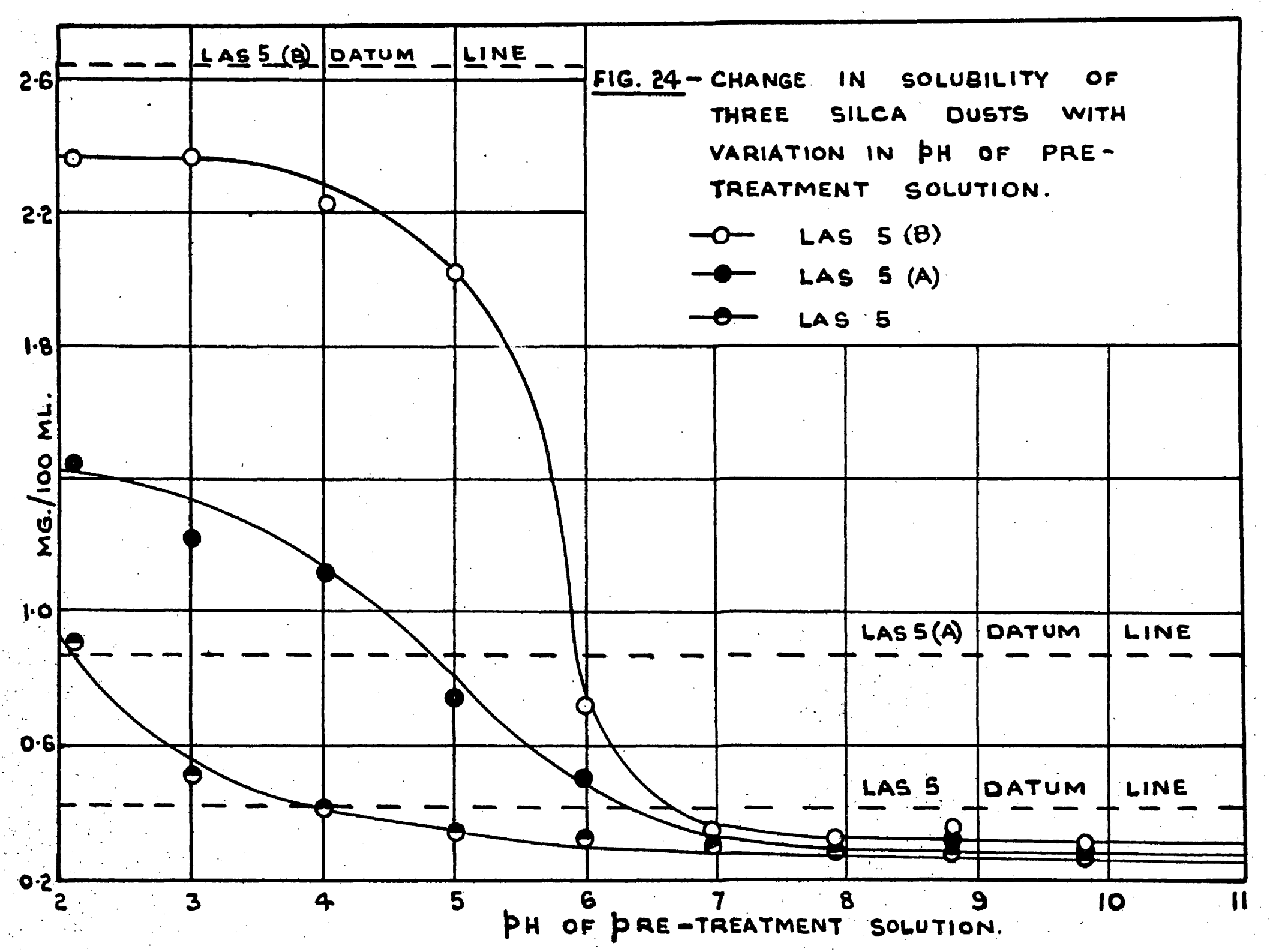

FIG. 24 – CHANGE IN SOLUBILITY OF THREE SILCA DUSTS WITH VARIATION IN PH OF PRE-TREATMENT SOLUTION.

LAS 5 (B)

LAS 5 (A)

LAS 5

/of the silicic acid from the particle surfaces, thus reducing the solubility in borate buffer. It is of interest that the minimum solubility reached by each dust (ca. 0.3 mg./100ml.) is virtually the same as that obtained on heating a similar dust at increasing temperatures (Fig. 21).

Clelland et al.[54] also observed that organic acids increase the solubility of Lochaline sand, but to a lesser extent than do the inorganic acids, which were of lower pH. These earlier results thus agree well with the present postu-:late.

From the foregoing considerations, it would be expected that after reduction, by heating, of the acid-enhanced solubility of a dust, further treatment by mineral acid would again increase the solution-rate. To investigate this possi-:bility, 4g. samples of LAS 5 were extracted for 48 hours with hydrochloric acid (pH 0.8) at 37°, washed thoroughly and dried at 37°. Table X (col. 3) shows the effect of various after-treatments on the enhanced solubility (3.75mg./100 ml.) of eight samples (A - H) of acid-treated Lochaline sand. With the exception of electrodialytic treatment (samples G, H), the after-treatments markedly decrease the dust solubilities. The effect of heat is again apparent (samples A,B); and treatment with alkali (samples C,D) has also markedly reduced the solu-:bility, an effect probably due to neutralisation of adsorbed ions and vigorous dissolution of silicic acid by potassium

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TABLE X.

Methods of reducing the solubility of acid-extracted Lochaline sand and the effect of a subsequent acid treatment.

Solubilities are expressed as mg./100 ml. after 48 hours in borate buffer (pH 7.5) at 37°; mass/liquid ratio, 4g./40 ml.

Initial solubility of acid-treated dust = 3.75 mg./100 ml.

Sample	1st Treatment	Solubility after 1st Treatment	Final Solubility
A	Heated at 490° for 3½ days	0.39	0.40
B	Heated at 1000° for 30 minutes	0.67	0.56
C	40 ml. N KOH for 48 hours	0.32	0.29
D	40 ml. N KOH for 48 hours	0.31	0.29
E	40 ml. distilled water for 17 days	0.17	0.17
F	40 ml. distilled water for 17 days	0.17	0.16
G	Electrodialysis for 4 hours	3.05	0.33
H	Electrodialysis for 4 hours	3.00	0.26

/hydroxide. A similar but milder reaction is evident after prolonged treatment with distilled water (samples E,F). Electrodialysis was employed (samples G, H) in an attempt to induce migration of adsorbed ions to a negative electrode immersed in a stirred suspension of the dust in distilled water. Only a small reduction in solubility occurred, a result pro-:bably attributable to the water alone.

After the above solubility estimations, each sample was washed in distilled water, dried at 37°, and further extrac-:ted with hydrochloric acid (pH 0.8) for 48 hours. After thorough washing of each dust, and drying at 37°, the solu-:bility was again estimated (Table X, col. 4). In each experiment, the observed failure to effect a further increase in solution-rate may be ascribed to the regeneration of inactive surfaces. Complete removal of impurities during initial extrac-:tion with acid may also be a contributing factor, since the solution-rate of a Lochaline-sand dust can be increased by acid treatment after extraction (30 days) with a borate buffer (pH 7.5).[54] Alumina, being amphoteric, will be only very slightly soluble at this pH, and the subsequent reaction with acid occurs, even after prolonged extraction with borate buffer.

Heat treatment has inactivated the particle surfaces, probably by closing the surface pores produced on removal of impurities. It is also known that if a montmorillonite dust, carrying hydrogen ions, is heated to high temperatures, the

/

/result is a complete remodelling of the crystal lattice, not simply a desorption of hydrogen ions[83].

This failure of acid-treated dusts to develop an increased solution-rate has a significance which will be dis-:cussed in Part 11(B).

Variation of the extent of solubility-reduction by heat.

To investigate further this effect of heating on the solubility of an acid-extracted dust, 4g. samples of LAS 5(C) were heated for different periods at constant temperature. The solubility of each sample was determined after 48 hours in borate buffer solution (pH 7.5) at 37° (mass/liquid ratio 4g./40 ml.), and results for three different temperatures are shown in Fig. 25. An equilibrium solubility is apparently reached after an initial rapid decrease. The point A is lower than would be expected, owing to an increase in furnace tem-:perature overnight, resulting from a decrease in mains load. This difficulty was obviated in subsequent runs by including a temperature-control unit in the furnace circuit, as can be seen from the corresponding points on the remaining curves.

It may be noted from Fig. 25 that the three samples of LAS 5(C) show slightly different initial solubilities. The three experiments (at 250°, 360°, and 480°) were commenced at intervals of some 10 days; and the decrease in initial solu-:bility observed probably provides another example of the effect of ageing a dust on its solubility, already shown by Clelland et al.[54].

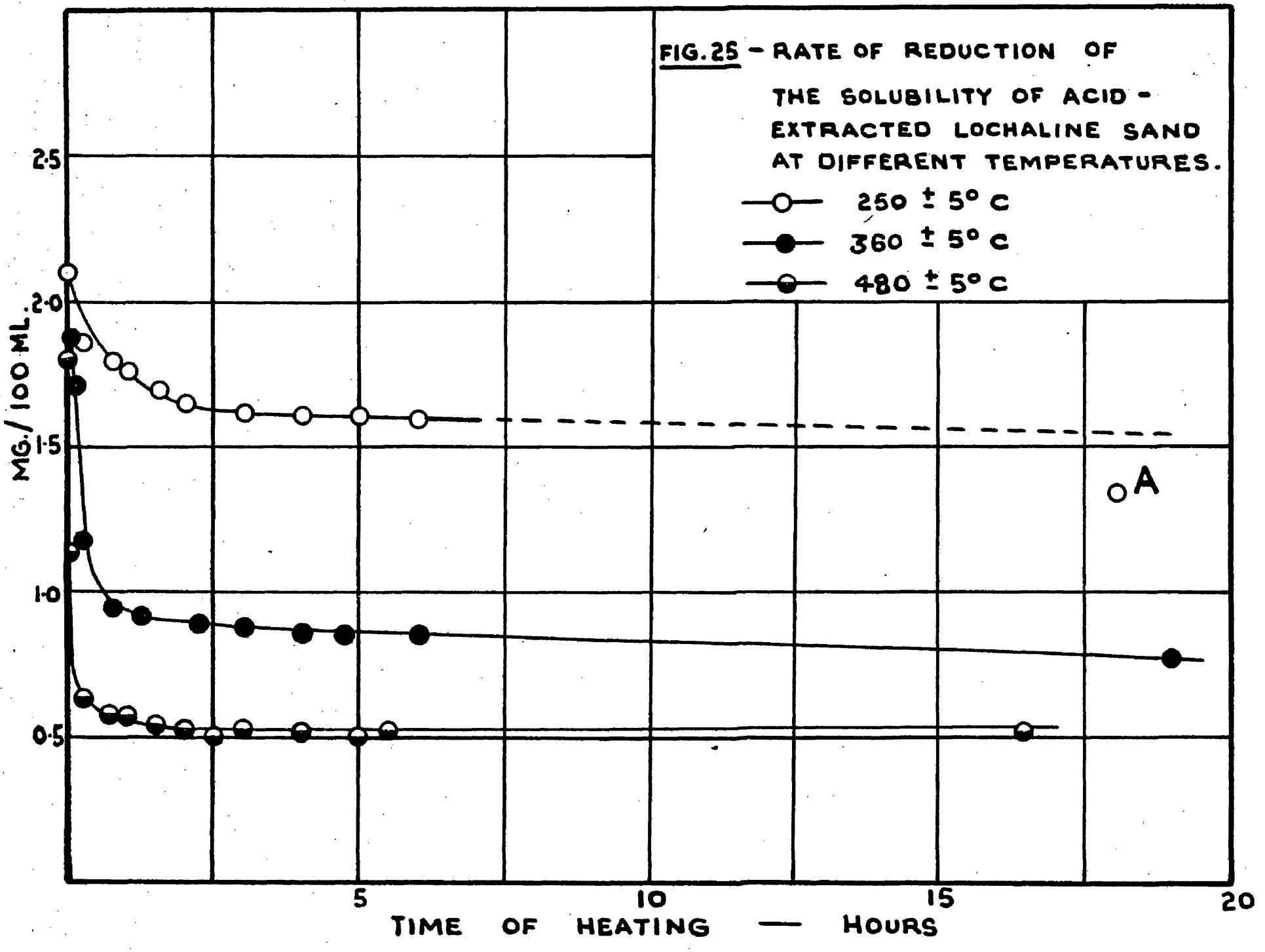
FIG. 25 - RATE OF REDUCTION OF THE SOLUBILITY OF ACID - EXTRACTED LOCHALINE SAND AT DIFFERENT TEMPERATURES.
250 ± 5° C
360 ± 5° C
480 ± 5° C
A
MG./100 ML.
2·5
2·0
1·5
1·0
0·5
5
10
15
20
TIME OF HEATING — HOURS

/ Although solubility is a rather arbitrary measure-:ment, a tentative kinetic analysis of the above curves has been made. A series of virtually coincident straight lines is obtained (Fig. 26) when the time of heating is plotted against $1/(a - x)$, where a = initial solubility minus an arbitrary equilibrium value, and x = decrease in solubility after time t (i.e. the extent to which the reaction has pro-:ceeded).

The arbitrary equilibrium values were chosen on the assumption that the change follows a second-order law. This required an asymptotic equilibrium value a, which cannot readily be measured directly, but which can be selected so as to give optimum linearity when t is plotted against $1/(a - x)$. Though the results (Fig. 26) show some scatter, this is inevitable in view of the nature of the experiment, but the linearity is better than that obtained by plotting other integral reaction-orders, and is sufficiently good to justify the above-mentioned assumption. In any case, the arbitrarily chosen equilibrium values of a are very nearly the same as the experimental values, so that this treatment of the results is simply a slight refinement.

The virtually coincident straight lines obtained (shown for simplicity as a single line in Fig. 26) implies a second-order reaction with a rate which is independent of tem-:perature. Completely analagous results were also obtained for/

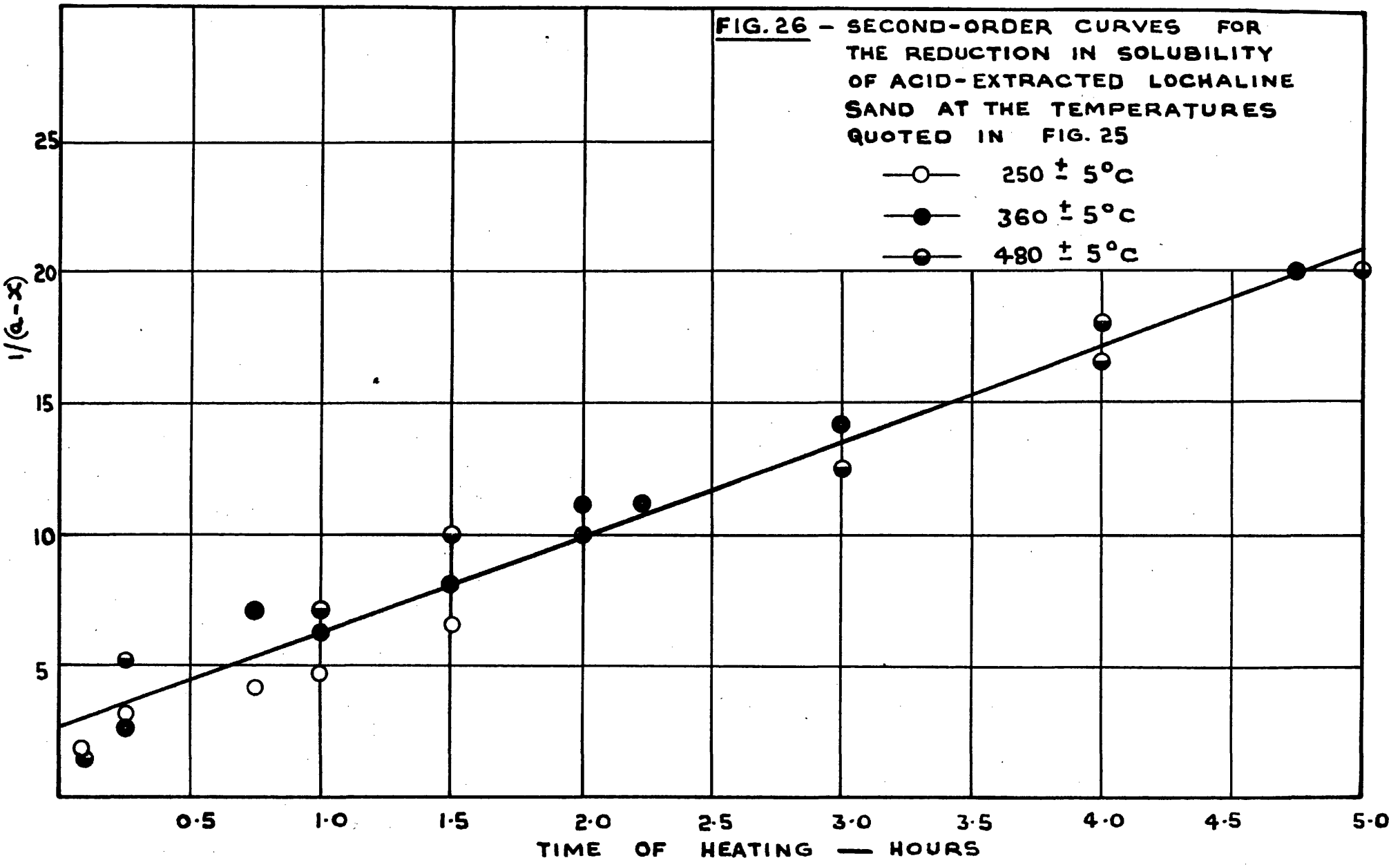
FIG. 26 – SECOND-ORDER CURVES FOR THE REDUCTION IN SOLUBILITY OF ACID-EXTRACTED LOCHALINE SAND AT THE TEMPERATURES QUOTED IN FIG. 25
250 ± 5°C
360 ± 5°C
480 ± 5°C
1/(a-x)
25
20
15
10
5
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
TIME OF HEATING — HOURS

/a Lochaline-sand dust submitted to a much more vigorous treatment with hydrochloric acid.

This equilibrium solubility is not the resultant of a forward and a backward reaction, since the dust is being heated in the atmosphere; and it is suggested tentatively that it is due to the presence of a system of protons and "discharged protons". As the particles are heated some adsorbed hydrogen ions become discharged, thus reducing the possibility of attraction of negative hydroxyl ions from the solvent, with consequent reduction in solubility. At increased temperatures, such ions may be not merely discharged but also liberated as elementary hydrogen, so that a new equilibrium is set up between the remaining ions and other "discharged ions", again resulting in a reduced solubility. This detailed picture is advanced with great reserve; its confirmation by direct observation of liberated hydrogen is necessary, though clearly a matter of great difficulty.

Infra-red absorption studies.

Hauser, Le Beau and Pevear[84] showed by infra-red spectrometry that sodium and calcium montmorillonites contain hydroxyl ions adsorbed on the particle surfaces. A band at 3700 $cm.^{-1}$ corresponds to a hydroxyl band such as is observed for hydroxides and water vapour; and a broader band at 3200 - 3600 $cm.^{-1}$ is characteristic of liquid water. Hauser et al. found that heating to 150° removes practically all

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/adsorbed water, but that heating even to 500° does not appre-:ciably affect the hydroxide content of the sample. Silica gel also shows a relatively sharp band near 3700 cm.$^{-1}$, the depth of the minimum increasing with decreasing particle size.

In contrast to these results, it has now been found that finely ground Lochaline sand, before and after acid extraction shows no hydroxyl band. This provides further evidence that the enhanced solubility of acid-treated silica dusts is not due to a hydrated surface such as is present on silica gel particles.

Hauser et al. also subjected dialysed montmoril-:lonite (carrying hydrogen ions) to infra-red studies, and observed a decrease in the amount of adsorbed water. When heated to 500°, hydrogen ions are not released in combination with hydroxyl groups as water. This would seem to support the present postulate that the reduction in solubility of acid-treated Lochaline-sand dust on heating should be attri-:buted to desorption of hydrogen ions alone, and not to release of water.

Base-exchange Capacity of impure silicious dusts.

On the basis of the foregoing results it would seem that the increase in solubility (and, possibly, pathogenicity) by mineral acid extraction of the silicious dusts examined is due to the formation of a surface layer of hydrogen ions. A simple ionic adsorption is the most obvious mechanism of the /

/reaction. Since the materials contain appreciable amounts of impurities, however, the possibility of a base-exchange reaction must be considered, and has been investigated experi-:mentally.

It has long been known that base-exchange capacity is an important property of soils, clays, and clay minerals. These materials possess the power of removing from solution small amounts of bases (e.g. ammonia, lime), and when a salt, such as potassium sulphate, percolates through a soil, some of it is removed and an equivalent quantity of calcium sulphate goes into solution. This phenomenon is now known as ion - or cation - exchange capacity since only ions are involved. The main factors determining base-exchange capacity are : pH, nature and concentration of reacting cation, and the time of interaction.

The concept developed by Mukherjee and Ganguly[85] defines base exchange capacity as the result of isomorphous replacement in the crystal lattice. Kaolin, showing no isomorphous replacement, has a capacity by virtue of "broken bonds" at the edges and exposed surfaces of the crystals. Quartz is similar to kaolin in this respect. Interchange not only occurs with salts, but with dilute acids, giving rise to hydrogen or acid systems whereby the original cations are replaced by hydrogen ions. The basis of the methods for determining base-exchange capacity is, in fact, the formation

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/of a hydrogen system and subsequent interaction with a second positive ion (e.g. potassium), followed by titration with alkali of the replaced hydrogen ions in solution.

It appears logical to expect that a similar reaction might occur when a finely ground impure silicious dust is extracted with dilute mineral acid. The solubility of these substances is known to increase, and if the presence of the hydrogen ions on the particle surfaces is due to a base-exchange reaction, solubility increase can occur by the pre-:viously postulated mechanism, i.e. by increasing the number of negative hydroxyl groups attracted to the particle sur-:faces and formation of more silicic acid.

To investigate this possibility samples of impure silicious dusts were extracted with mineral acid, solubility increases estimated for each material, and base-exchange capa-:cities determined.

Experimental.

Samples of sandstone, olivine, orthoclase, Lochaline sand, and quartz were prepared as described previously and ground overnight in an agate mortar. DRC silica and kaolin were obtained commercially.

A large number of methods for determining ion-exchange capacity are available owing to its ill-defined nature. Since comparative results were required in this experiment, it was necessary to use only one method. The pro-:cedure adopted was a development of the sulphonic acid method

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/of Kunin and Myers[86] and the KCl/KOH method of Ganguly[87].

Hydrogen systems were prepared by extracting two 3g. portions of each dust with 40 ml. of N/10 hydrochloric acid for 72 hours at 37°. The solids were separated by fil-:tration through three thicknesses of filter paper. After thorough washing with distilled water until the filtrate was neutral to methyl orange, the samples were dried at 37°. 3g. of each acid-extracted dust was weighed accurately in a flask and suspended in 25 ml. of distilled water, and an equal volume of half-saturated potassium chloride solution added. The flasks were stoppered and the suspensions left standing for 18 hours with occasional shaking. The liquids were then separated by filtration through a Whatman No. 542 filter paper, and 25 ml. of each titrated with N/10 sodium hydroxide using phenolphthalein as indicator.

The results are shown in Table Xl, and are expressed as milliequivalents of cation per 100 gm. of solid. Solu-:bilities of the material before and after acid extraction were determined in borate buffer solution (pH 7.5) after 48 hours at 37°, mass/liquid ratios 0.2g./40 ml. There is apparently no correlation between the increase in solubility brought about by extraction with mineral acid and the ion-exchange capacity for the impure silicious dusts examined. These materials possibly fall in line with quartz and kaolin in that their low base-exchange capacities are due to attachment of

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TABLE X1.

Ion-exchange capacities and solubilities of seven silicious dusts.

Sample	Solubility before extraction (mg./100 ml.)	Solubility after extraction (mg./100 ml.)	Increase in solubility (mg./100 ml.)	Ion-excha capacity (m.equiv./ 100g
DRC silica	0.86	2.92	2.06	2.04
Sandstone	1.08	8.10	7.02	0.62
Olivine	2.60	3.56	0.96	0.37
Orthoclase	0.92	9.70	8.78	1.02
Lochaline sand	2.80	5.68	2.88	-
Quartz	5.40	4.00	-	0.99
Kaolin	0.39	0.46	0.07	1.91

/ions at "broken bonds" at the crystal surfaces and edges.

It is thus apparent that the increase in solution-rate of an impure silicious dust by hydrogen ion adsorption is not a result of isomorphous replacement of the cation impurities (by hydrogen ions) in the crystal lattice. Quartz has a measurable exchange capacity but fails to exhibit a solubility increase on acid treatment. Thus it is very pro-:bable that the increase in solubility shown by the other samples is merely due to ionic adsorption on the particle surfaces and not to an ion-exchange mechanism. The base-exchange reaction does not play a significant part in effec-:ting an increase in solubility since quartz has a base-exchange capacity almost equal to orthoclase, for example, while the solubility of quartz is reduced, and that of ortho-:clase markedly increased, by the formation of a hydrogen system.

Notes on nomenclature.

Earlier in the published series of this work[54,55] the highly-soluble surface layer on silicious dust-particles was denoted by the term "HS (= high-solubility) layer". It soon became apparent that, for certain dusts, high solubility may be induced by more than one method (e.g. mechanical grinding or polishing, and treatment with acids), and it was pointed out[56] that the new surfaces thus produced are not necessarily, or even probably, identical. Since it is clearly

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/undesirable to use a single term to describe what are probably different phenomena, the use of the term "HS layer" was discontinued; and it is proposed to use in its place the terms "disturbed layer" (to denote a surface produced by mechanical processes such as grinding and polishing) and "X-modified layer" (to denote an altered surface produced by some other agency X - for example, "acid-modified layer"). Further subdivisions of nomenclature may become necessary as the work proceeds. For example, there is already some evidence that the disturbed layer itself may be composite, consisting of an outer layer of small fragments adhering to the main underlying amorphous layer, and that this in turn blends via a cryptocrystalline transitional layer into the truly crystalline substrate.

Conclusions.

(1) Extraction of orthoclase, olivine, sandstone, DRC silica, and Lochaline-sand dusts with hydrochloric acid increases the silica-solubility. This enhanced solution-rate can be decreased by heating; and DRC silica and Lochaline sand recover their original solubilities after being heated for thirty minutes at about 900°.

(2) The solubility of a ground pure-quartz dust is reduced by acid treatment, an effect best accounted for by the dissolution of a portion of the disturbed layer during extraction. Alumina is removed from DRC silica and Loch-

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/:aline-sand dusts during acid extraction; and, since alumina is known to depress silica-solubility, this might well be enhanced by removal of alumina. This effect, however, has been found to be only partially responsible for the increased solution-rate.

(3) After heating a sample of acid-extracted Lochaline sand the solubility does not again increase on acid treatment. Similarly, neither pre-treatment with alkali or distilled water, nor electrodialytic treatment, regenerates this active surface.

(4) Hydration of silica surfaces does not occur during acid treatment, but the extent to which the solubility is raised is markedly dependent on the pH of the acidic medium. The pH of solutions of sulphuric acid was found to increase after extraction of samples of Lochaline sand. It is thus concluded that the increase in solution-rate of such impure silicious materials is due to adsorption of hydrogen ions from the extracting solution, on the surface irregularities pro-:duced by the removal of alumina and other impurities. The presence of these ions enables the silica surfaces to attract a greater number of negative hydroxyl groups from the solvent medium, with subsequent formation of highly soluble silicic acid. It has already been pointed out that the solution-:rate of acid-treated Lochaline sand is reduced to its pre-:treatment value by a solution period of approximately three days, but a period of 20 days was required to reduce the

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/initial solution-rate due to dispersion of the disturbed sur-:face-layer. This earlier result of Clelland et al.[54] is significant in the light of the foregoing results, since the presence of a layer of adsorbed hydrogen ions on the particle surfaces, after acid extraction, forms silicic acid very readily, markedly increasing the dispersion-rate of the sur-:face-layers.

(5) Adsorption of hydrogen ions on the surface of silicious dust particles is ionic in nature and is not due to isomorphous replacement of cation impurities in the crystal lattices, although the minerals examined exhibit measurable ion-exchange capacities.

B. Some Sorption Properties of Silicious Dusts.

Introduction.

The disturbed layer on silica particles, produced during crushing and grinding has a marked effect upon their solution-rates[54]; and it was considered likely that this layer might also in some measure control the process of adsor-:ption at the dust particle surfaces. Further, it has been concluded that the enhanced solubilities shown by impure silica dusts on extraction with mineral acid were due to adsorption of hydrogen ions on the particle surfaces; and it seems likely that this process, also, may influence the subsequent adsorption of another cation. Confirmation of any such effect would give valuable support to the ideas previously advanced.

The following experimental work was designed, there-:fore, to determine whether prior removal of the disturbed layer of amorphous silica from the surfaces of different sili-:cious dust particles has any effect on the adsorption of a suitable ion, and whether acid extraction of an impure silicious dust depresses its adsorptive properties. Modified surface-:layers on dust particles may play an important role in their pathological reactions with lung tissue, and any differential adsorption effects would be a useful pointer towards future work on pathogenic airborne dusts.

EXPERIMENTAL.

Materials: Source and preparation of dusts. /

(i) Rock crystal dust (125 - 200μ) was prepared by reducing selected quartz crystals in a steel jaw-crusher and roller mill. The sieved 70 - 90 - mesh fraction was extracted with concentrated hydrochloric acid to remove iron contamination, thoroughly washed, sedimented from water to remove particles less than 125μ, and dried at 120°.

(ii) Lochaline-sand dust LAS 5 (125 - 475μ) was prepared from the natural sand by repeated sedimentation from distilled water to remove all particles less than 125μ, and dried at 120°.

(iii) Vitreous silica dust (125 - 200μ) was prepared by crushing transparent Vitreosil (99.8% silica) in a steel roller-mill. The product was sieved, extracted, washed, and dried exactly as for rock crystal.

Particle-size ranges were measured microscopically using a calibrated graticule.

Removal of surface layers.

To remove the disturbed layer from rock crystal and Vitreosil dusts, these were treated with 40% hydrofluoric acid for 10 and 5 minutes respectively, the Vitreosil reacting more vigorously than the quartz. The acid was diluted and, after thorough washing, the dusts were dried at 120° for 18 hours. Since acid treatment of Lochaline sand increases its rate of solution, this dust was freed from its surface layer, not by means of acid, but by agitating 4g. quantities with 40 ml. of

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/borate buffer solution (pH 7.5) in Lusteroid tubes for 24 days at 37°.

The solubilities of all the dusts were then deter-:mined and it is apparent from the results (Table XII) that the treatments have removed a highly soluble layer from the particle surfaces.

Choice of adsorbate.

For the sake of easy colorimetric determination, a dyestuff was chosen, the following classes of dyes being tested for suitability: Vat, direct cotton, acid, basic, and sulphur dyes. 10% solutions of various dyes from each cate-:gory were shaken with a standard weight of Lochaline-sand dust, and it was found that only basic dyes are appreciably adsorbed. From this restricted category, Methylene Blue was chosen since it is available in a very pure state (B.P. quality).

Mechanism of adsorption: determination of adsorbate.

Basic dyes such as Methylene Blue owe their colour in solution to a "colour cation". The fact that only basic dyes are adsorbed by silica, coupled with the fact that silica particles, in aqueous suspension bear a negative charge(except in intensely acid media[88]), suggests that the observed adsorp-:tion is due to electrostatic attraction between the silica surface and the "colour cation". It is of interest that the adsorption of amino acids and dipeptides by silica dusts appears to be due mainly to a similar ionic process[89].

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TABLE XII.

Solubility of rock crystal, Vitreosil, and Lochaline sand in borate buffer (pH 7.5) at 37°; mass/liquid ratio, 4g./40 ml.

Sample	Time of contact with solvent (days)	mg./100 ml.
Rock crystal :		
Untreated	8	1.26
Treated	8	0.76
Vitreous silica :		
Untreated	8	2.34
Treated	8	1.62
Lochaline sand :		
Untreated	6	0.95
Treated	6	0.34

The dye used was of B.P. quality; its purity, determined by the method described in the British Pharmacopoeia[90], was 83%. A weighed amount was dissolved in water and suitably diluted to give a reading on the most accurate portion of the logarithmic scale of an EEL colorimeter (i.e. 40 - 50 units), using a red Ilford filter (No. 608). The optimum initial concentration was found to be 2.96 mg./l.

A series of solutions of known concentrations was prepared from this standard by dilution. The plot of colorimeter reading vs. dyestuff concentration gave a linear calibration curve, from which it was found that a decrease in colorimeter reading of 20 scale-divisions was equivalent to a reduction in dye concentration of 1.25 mg./l. Hence, to reduce by 1 unit the colorimeter reading given by 10 ml. of dye solution requires the adsorption of 0.195×10^{-8} g. mole of $C_{16}H_{18}N_3S\,Cl$.

Adsorption procedure.

1 g. quantities of rock crystal and vitreous silica and 0.25 g. quantities of Lochaline sand were weighed into a glass colorimeter tube, 10 ml. of adsorbate solution added, and the whole closed with a cork coated with paraffin wax. Periodic colorimeter readings were taken, the dusts being shaken with the solution at the end of each reading, until equilibrium was reached. The dusts settled rapidly and the design of the colorimeter was such that passage of light

/through the solution was not affected by the sample at the bottom of the tube. The difference between "blank" readings (i.e. dust omitted) and the average of duplicate dust tests was multiplied by the factor 0.195, giving the amount of dye adsorbed (g. mole x 10^{-8}). Tests were carried out with quartz, vitreous silica, and Lochaline-sand dusts, each of them with and without the disturbed layer.

The results (Figs. 27 and 28) show that untreated Lochaline sand displays the greatest affinity for Methylene Blue and vitreous silica the least. It is evident that the activity of Lochaline-sand surfaces in adsorption processes differs from that in solution processes, for although this dust has a much greater affinity for the dye, it has a much lower solubility than either rock crystal or vitreous silica.

It is clear from Figs. 27 and 28 that removal of the disturbed layer from all three dusts has decreased the amount of adsorption. This effect cannot be due simply to a reduction in particle size by extraction with hydrofluoric acid and borate buffer solution, since this would tend to increase (i) the specific surface of each dust, and hence (ii) the equilibrium adsorption. It must, therefore, be con-:cluded that for these three dusts the disturbed layer has a greater affinity for the adsorbate than the underlying core.

This result is understandable, though perhaps not predictable with certainty, for crystalline materials such as

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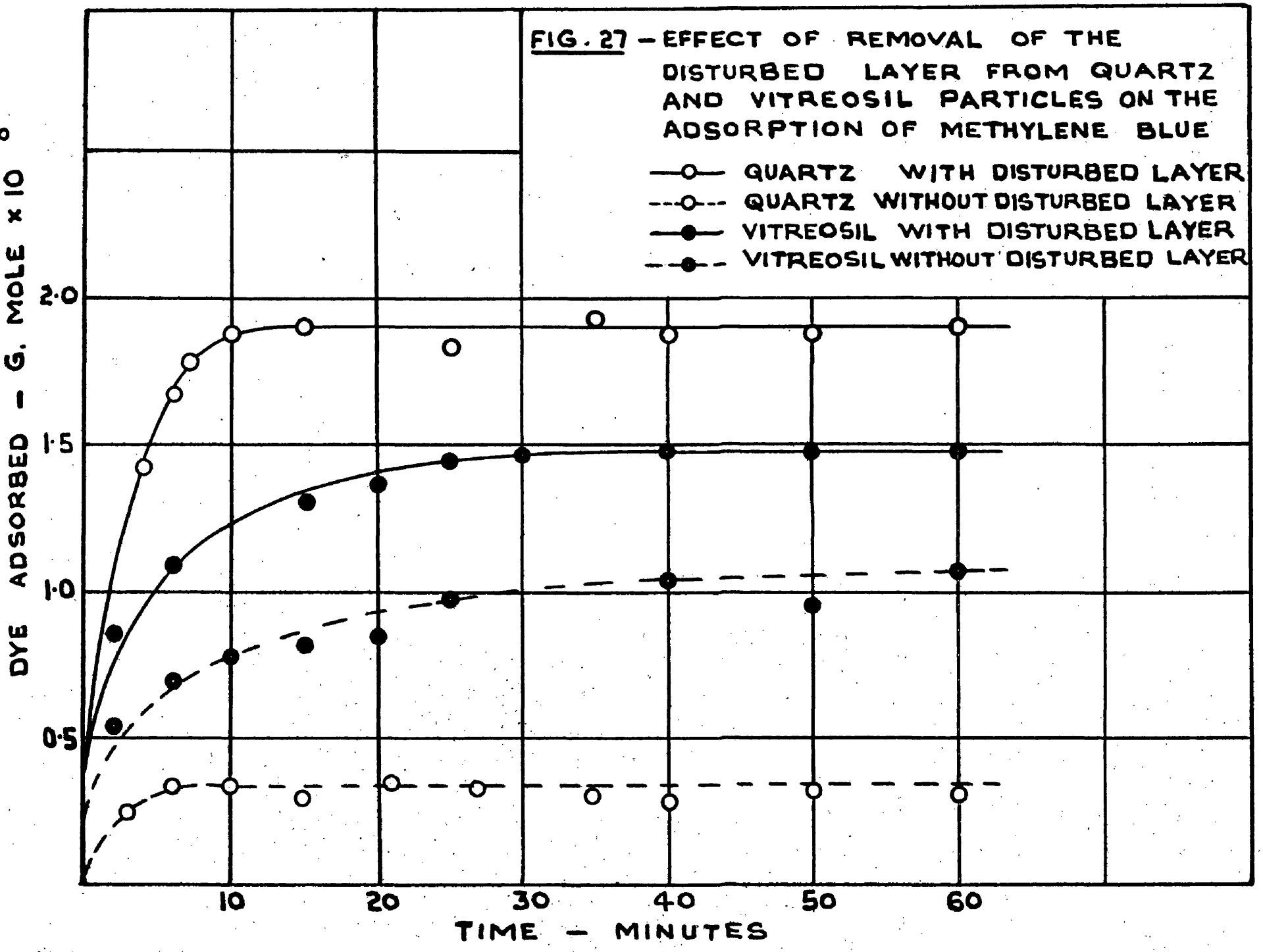
FIG. 27 – EFFECT OF REMOVAL OF THE DISTURBED LAYER FROM QUARTZ AND VITREOSIL PARTICLES ON THE ADSORPTION OF METHYLENE BLUE
QUARTZ WITH DISTURBED LAYER
QUARTZ WITHOUT DISTURBED LAYER
VITREOSIL WITH DISTURBED LAYER
VITREOSIL WITHOUT DISTURBED LAYER
DYE ADSORBED – G. MOLE x 10⁻⁸
2·0
1·5
1·0
0·5
10
20
30
40
50
60
TIME – MINUTES

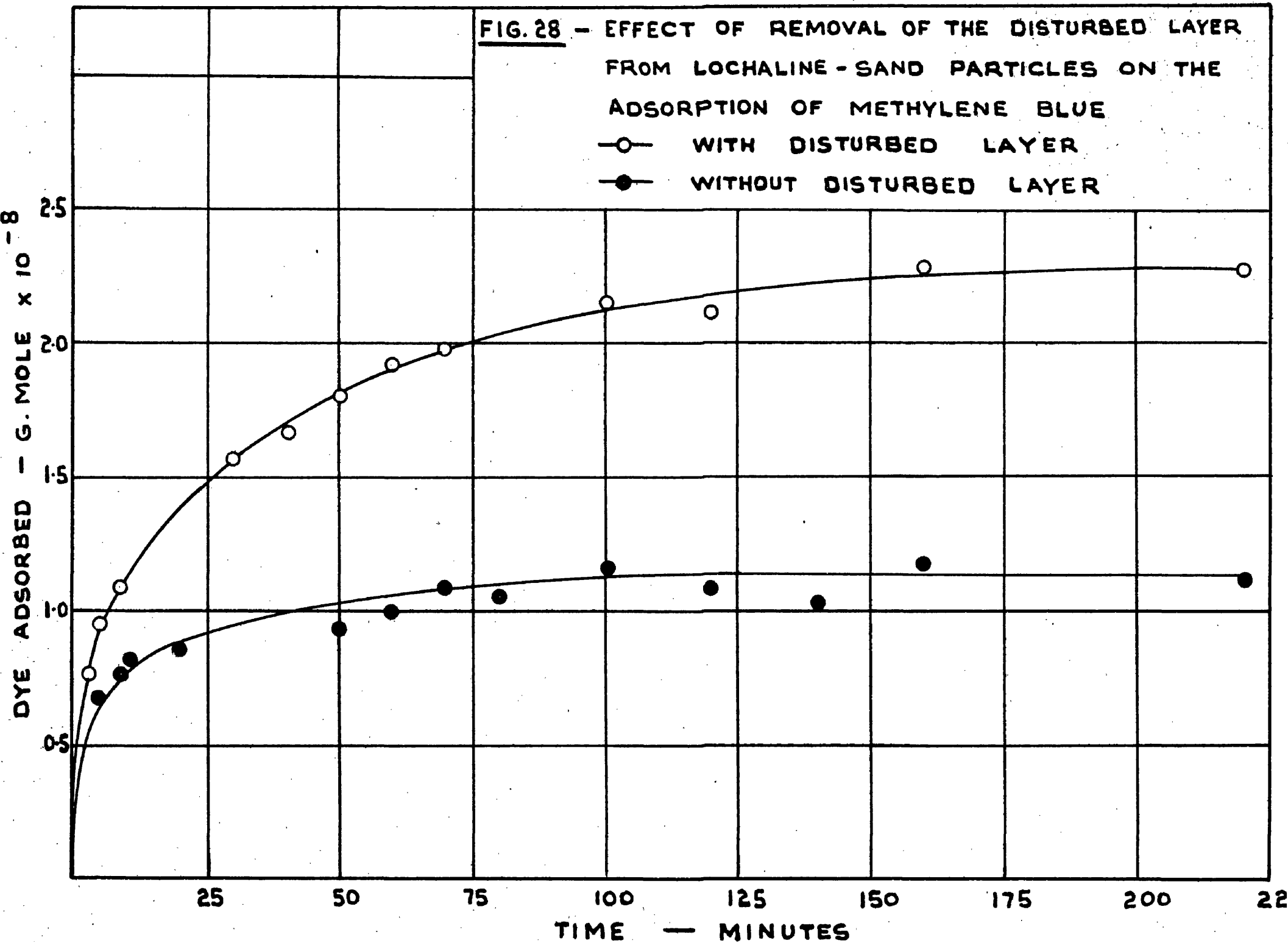
FIG. 28 – EFFECT OF REMOVAL OF THE DISTURBED LAYER FROM LOCHALINE-SAND PARTICLES ON THE ADSORPTION OF METHYLENE BLUE
WITH DISTURBED LAYER
WITHOUT DISTURBED LAYER
DYE ADSORBED – G. MOLE x 10 – 8
2·5
2·0
1·5
1·0
0·5
25
50
75
100
125
150
175
200
TIME — MINUTES

/rock crystal and Lochaline sand; but it is more surprising for Vitreosil, which is normally assumed to be wholly amor-:phous, so that the disturbed layer and the underlying core would not here be expected to show different adsorptive powers. It seems necessary to assume some physical difference between layer and core to account for the difference in adsorption. It may well be, for example, that the crushing of massive Vitreosil produces an amorphous surface-layer with the struc-:ture more open than that of the core. Alternatively, there is a possibility that the disturbed layer on Vitreosil may be truly amorphous, whereas the "amorphous" core may still retain vestigial zones of organised structure, or minute crystallites of cristobalite, as previously suggested[56] to account for the allied fact that a highly soluble surface-layer is generated by polishing not only quartz but also Vitreosil dusts with a suitable mild abrasive. Finally, it is possible that the physical picture of the disturbed layer which has been drawn in earlier work requires modification.

Effect of acid treatment and heat treatment on adsorption.

It has been observed that the solution-rate of impure silica dusts may be increased by acid treatment, pre-:sumably owing to adsorption of hydrogen ions on the acid-modified surface created by removal of impurities. It might be expected, therefore, that the rate of adsorption of Methy-:lene Blue would be greatly reduced by the presence of ions

/

/of like charge on the surface of an acid-extracted dust. Furthermore, the solubility of a silica dust is greatly reduced after heating, and cannot be again increased by further extraction with acid; and if heat treatment similarly affects the equilibrium adsorption of Methylene Blue by an acid-treated Lochaline-sand dust, this would clearly support the concept outlined in Part 11(A).

LAS 5(E) was prepared by treating 50 g. of LAS 5 with 200 ml. of N hydrochloric acid at room temperature, washing thoroughly, and drying for 48 hours at 37°. Three 4 g. portions of LAS 5 were agitated for 72 hours, each with 40 ml. of hydrochloric acid of different pH value (1.70, 0.95, and 0.75). The dusts were washed until free from acid, and dried at 37°. Adsorption experiments (Fig. 29) were carried out using 0.25 g. quantities of these three dusts, as well as of LAS 5 and LAS 5(E).

LAS 5(F) was prepared by agitating 20 g. portions of LAS 5 for 90 hours with 35 ml. of N hydrochloric acid at 37°. After thorough washing, the material was dried for 48 hours at 37°. LAS 5(F) was heated at 685° for 18 hours; adsorption experiments (Fig. 30) were then performed with this material, together with LAS 5 and LAS 5(F).

The results show that extraction of Lochaline sand with hydrochloric acid has decreased the extent of adsorption at the particle surfaces, and that the rate of adsorption

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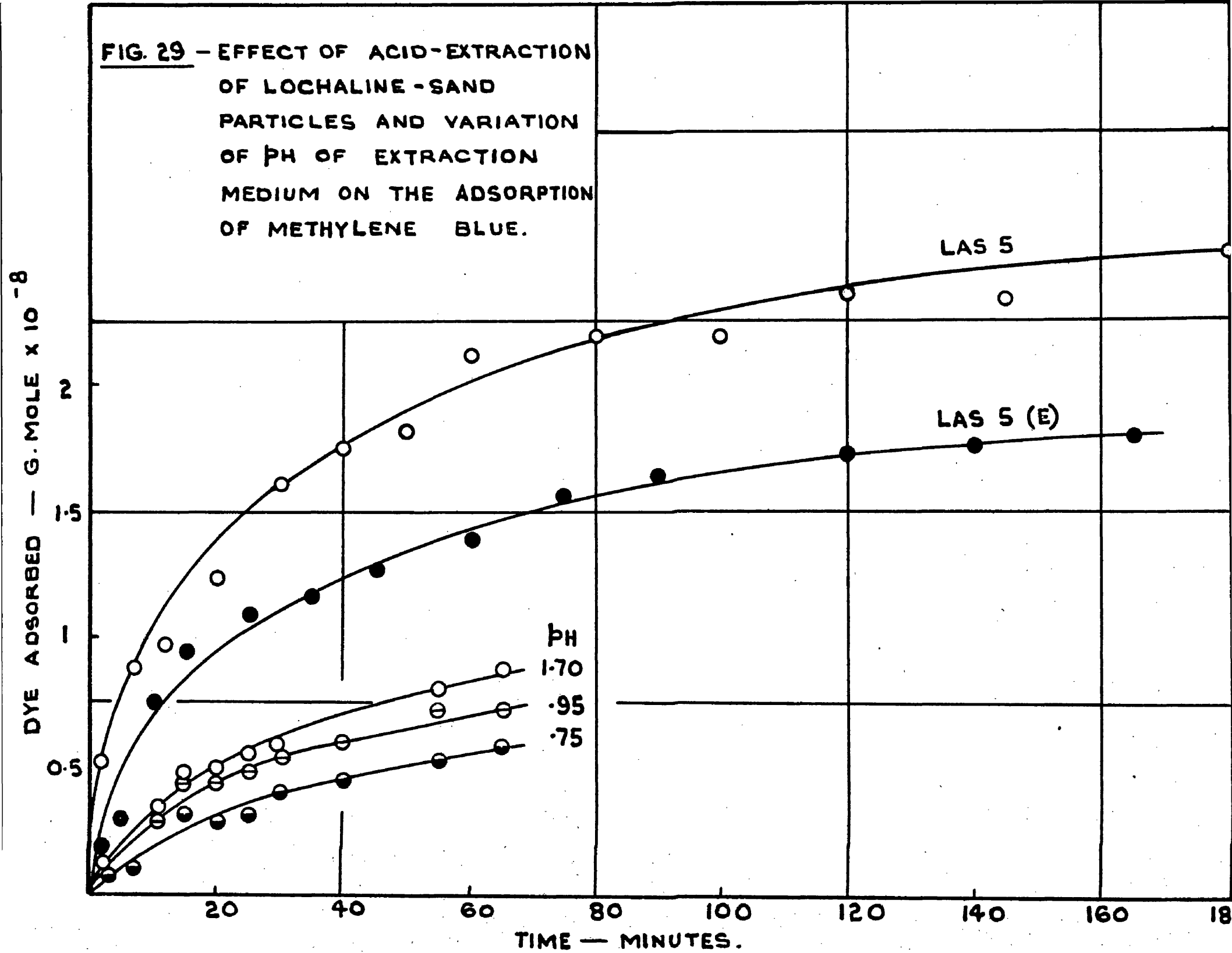
FIG. 29 – EFFECT OF ACID-EXTRACTION OF LOCHALINE-SAND PARTICLES AND VARIATION OF pH OF EXTRACTION MEDIUM ON THE ADSORPTION OF METHYLENE BLUE.
LAS 5
LAS 5 (E)
pH
1·70
·95
·75
DYE ADSORBED — G. MOLE x 10 -8
0·5
1
1·5
2
20
40
60
80
100
120
140
160
18
TIME — MINUTES.

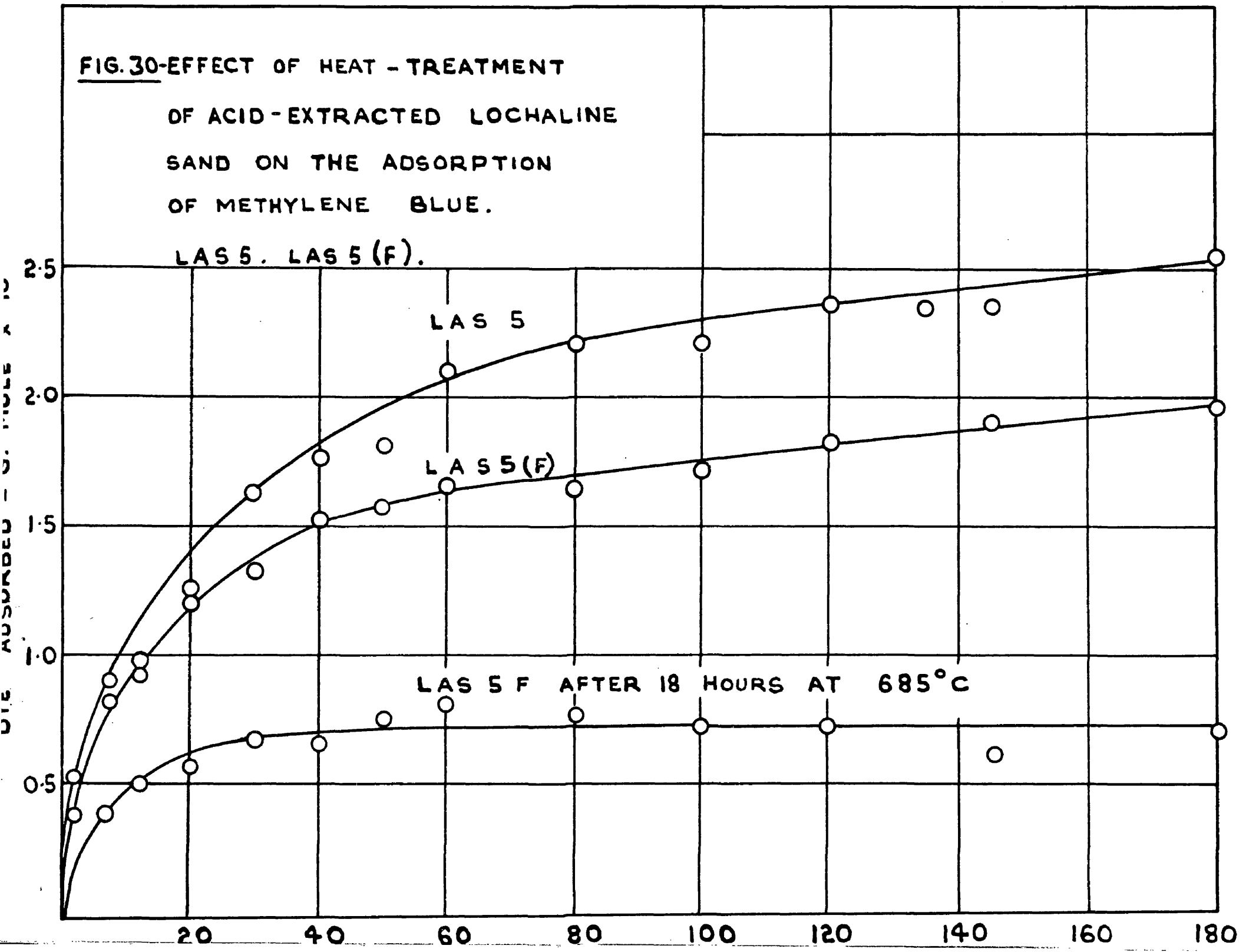
FIG. 30-EFFECT OF HEAT-TREATMENT OF ACID-EXTRACTED LOCHALINE SAND ON THE ADSORPTION OF METHYLENE BLUE.
LAS 5. LAS 5 (F).
LAS 5
LAS 5 (F)
LAS 5 F AFTER 18 HOURS AT 685°C
2·5
2·0
1·5
1·0
0·5
20
40
60
80
100
120
140
160
180

/decreases with decreasing pH of the extracting acid (Fig.29). It may be deduced from the results of Part 11(A) that this pH determines the number of hydrogen ions already present on the surface of the dust particles prior to adsorption of Methylene Blue. As the pH decreases, however, the rising concentration of hydrogen ions will depress the adsorption of dyestuff cations owing to increased repulsion of like charges and, possibly, a size effect.

The rate and extent of adsorption of Methylene Blue on acid-extracted Lochaline sand are markedly decreased after heating the dust (Fig. 30). The fact that heat treatment has been shown to decrease both the solubility of an acid-extracted Lochaline-sand dust and the extent of adsorption thereon of a positive ion seems to support the previous con-:clusion that the initial increase in solution-rate is due to adsorption of a cation from the extracting medium.

Conclusions.

(1) Rock crystal, Lochaline sand, and vitreous silica (Vitreosil) dusts all show reduced affinity for a dyestuff cation on removal of the disturbed outer layer from the par-:ticle surfaces. This layer of amorphous silica is there-:fore more reactive than the underlying core in sorption pro-:cesses, just as in solution processes.

(2) To account for this apparently anomalous behaviour of Vitreosil dusts it must be assumed that there is a dif-:ference(probably physical) between the amorphous outer layer

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/and the nominally amorphous core. It is suggested that the former may possess a more open structure.

(3) Acid-extracted Lochaline-sand dust has a lower affinity than the natural material for the dyestuff cation. This result lends precision to the concept of adsorption of hydrogen ions during the acid treatment, their presence having a depressing effect on subsequent adsorption of dye.

(4) Heat treatment of an acid-extracted dust has the same effect in both sorption and solution experiments. This again suggests that adsorption of hydrogen ions may be respon-:sible for the observed increased solution-rate of impure sili-:cious dusts. Since solubility is not further increased by a second acid extraction after the heat treatment, the latter process must alter the nature of the particle surfaces.

(5) Heat treatment in these sorption experiments was effected at a much lower temperature (685°) than in the pre-:vious solubility experiments. It is thus not unreasonable to assume that heat treatment at higher temperatures will reduce the equilibrium adsorption still further.

PART 111.

REGENERATION AND RECRYSTALLISATION OF THE AMORPHOUS LAYER ON SILICIOUS DUST SURFACES.

Introduction.

The effect of polishing on the properties of metal and non-metal surfaces has been a subject of considerable research for many years. The first recorded hypothesis on the nature of the process is to be found in the work of Hooke[91], who showed that the operation of grinding with an abrasive merely formed grooves which, he postulated, also resulted from surface polishing. Herschel[92] supported this concept and maintained that the size of the grooves was below the limit of resolution of the light microscope and so could not be observed. Between 1902 and 1921, Beilby[93] completed a thorough microscopic examination of the effects produced by polishing a large number of materials, and concluded that a vitreous-like skin is formed during the polishing of crystalline substances. Etching experiments resulted in the formation of the crystalline substrate once again and in variation of solu-:bility values. He also postulated the formation of an amor-:phous layer when two crystal faces were rubbed together, thus providing an explanation of the phenomenon known as 'cold-working' in the process of metal hardening. He attributed this to the formation of an amorphous layer between sets of slip planes, thus acting as a cementing material and pre-:venting further slip.

With the advent of the electron-diffraction camera, however, came an admirable method for the investigation of the structure of thin surface films by the scattering of

/

/electrons. Using this technique, Thomson[94] was unable to obtain diffraction patterns of such metals as gold, lead, iron, aluminium, and copper; he pointed out that this was due to a surface layer of amorphous material impenetrable to electrons. French[95] expanded this work by investigating the change in structure of a crystalline surface with increasing degree of polish. Sharp diffraction rings from the origi-:nally crystalline surface became more diffuse as polishing continued, until the diffraction effects produced by the core were completely obliterated by a halo pattern on a diffuse background. Germer[96], on the other hand, maintained that this disturbed layer was crystalline, since he obtained a general scattering of electrons from polished surfaces, and he attributed this to the surface being levelled in such a way that the electrons entered and left through the same crystal face.

An experiment which has apparently left no doubt as to the existence of the Beilby layer was performed by Finch, Quarrell and Roebuck[97]. They observed that the disturbed layer produced by polishing a metal surface, is capable of dissolving crystals of another metal at room temperature. Immediately upon deposition of a crystalline zinc film on a highly polished copper substrate (in the diffraction camera) the well defined diffraction pattern corresponding to zinc appeared. This pattern, however, lasted only for a few seconds, showing that the crystalline deposit had been destroyed.

/

/As successive layers of zinc were deposited the diffraction patterns were visible for increasing periods. The pattern from the twelfth deposit lasted for 4 hours. With a crystal-:line substrate (e.g. etched copper), on the other hand, a single zinc film showed neither change in brilliancy nor appearance during the 1½ hours for which it was observed.

Observations bearing directly on Beilby's hypothesis have been made by Desch[98]. He pointed out that the chemical activity of the disturbed layer is greater than that of the underlying crystalline material, and that the layer is anodic to the substrate. The density of the layer is less than that of the substrate, - a result to be expected since the random arrangement of molecules in the amorphous material occupies a greater space than does symmetrical packing. Bowden and Hughes[99] advanced their theory that one of the most important phenomena occurring during this process of polishing is what they describe as '.....an intense local heating at the points of contact. The melted or softened solid flows or is smeared over the surface and very quickly solidifies to form the characteristic Beilby layer'.

Some results have been obtained more recently by Clelland and Ritchie[55]. They found that, on polishing crystal-:line silica particles (from which the disturbed layer had been removed) with either silicon carbide or fine rock crystal dust, the rate of solution of silica was increased many times;

/

/the silica liberated into solution from the disturbed layer was mainly in the colloidal form. Since this effect is similar to that occurring during the initial stages of extractive solubility tests on a silicious dust carrying a disturbed layer (produced by crushing and grinding) these workers concluded that an effect of polishing is to regenerate this disturbed layer, which is, in fact, the Beilby layer. It appears from their results, however, that the disturbed layer produced by polishing was extremely thin, since solu-:bility/time curves quickly regained their initial low gradient (just prior to polishing) representing complete removal of both disturbed layers. At first sight, this would seem to indicate a difference in the solution properties of the two surfaces. It is possible that maximum solubility had not been reached by the polishing process; to enable a complete comparison of the two layers to be made more points would thus be required on the initial portion of the curve representing dispersion of the regenerated layer.

The following work was designed to provide further evidence for the similarity of the disturbed layers by chemical and physical methods. Solubility, adsorption, and electron diffraction techniques were employed to shed further light on the surface structure of polished crystalline and amorphous silica.

EXPERIMENTAL.

/

/EXPERIMENTAL.

Materials : Source and preparation of dusts.

The samples used are referred to by letters and a number signifying a particular batch. Particle size analyses were carried out as in the previous section.

Lochaline sand, LAS 5. - This material was described in Part 11, and the original batch was used throughout.

Amorphous silica, VT2 (130 - 220μ : $(\Sigma d)/n$ = 175μ). - A sample of transparent Vitreosil was ground in a Christy-Norris hammer-mill using a $\frac{1}{4}$ in. screen. The material was sieved and the 70 - 90 - mesh fraction extracted with concentrated hydro-:chloric acid to remove impurities (from the grinding process), washed thoroughly with distilled water, and dried at 120° for 5 hours.

Rock crystal, RC 1 (120 - 200μ : $(\Sigma d)/n$ = 180μ). - Madagascar quartz crystals, selected for transparency and freedom from occluded impurities, were ground as described above, and the 70 - 90 - mesh fraction treated in the same manner.

Removal of the disturbed layer.

This was accomplished by treating samples of VT 2 and RC 1 with 40% hydrofluoric acid for periods of 5 minutes and 30 minutes respectively. The samples were washed thoroughly with distilled water, and dried at 120° to give dusts RC 1(A) and VT 2(A). The layer was removed from the sample of LAS 5 by agitating 4 g. quantities with 40 ml. of borate buffer solution (pH 7.5) at 37° for 24 days. The dust was then /

/washed free from buffer solution and dried at 120°.

Factors affecting the solubility of a polished dust.

1. Time of polishing.

Before a comparison of the solution properties of both types of disturbed layer on crystalline and amorphous silica was made, it was considered necessary to ensure that, during subsequent polishing experiments, the polish layer had reached a maximum thickness. The time of polishing is obviously an important factor here and an example of the need for this condition of maximum thickness will be seen later. The following experiments were designed, therefore, to correlate time of polishing and resultant solubility.

Polishing agent. - A finely ground rock crystal dust was employed, and prepared by grinding 10 g. batches of RC 1 for 18 hours in a mechanical agate mortar.

Polishing treatment.

4 g. quantities of LAS 5 (disturbed layer removed), RC 1(A), and VT 2(A) were each mixed with 5 g. of polishing agent in 2 oz. glass bottles, closed with screw-cap lids and rotated at 30 r.p.m. for periods ranging from 2 to 25 days. During this process, complete and continuous contact is ensured between the abrasive and the dust particles. At the end of each polishing period the dusts were separated by repeated sedimentation from distilled water and dried at 37°. This drying process has been shown to have no effect in regenerating a high solution-rate after removal of the /

/disturbed layer[54]. Thorough examination in the light micro-:scope revealed no trace of residual polishing agent on the dust particles.

The solubilities of the dusts were determined after 48 hours in borate buffer solution (pH 7.5) at 37° (mass/liquid ratio 4g./40 ml.), and the results are shown in Fig.31.

It can be seen that, for each silica dust, a maxi-:mum solubility is reached after about 15 days polishing under the above conditions. This time of polishing will ensure the formation of a layer of maximum thickness, assuming layer thickness to be proportional to solubility.

2. The nature of the polished substrate.

It is purely a matter for conjecture at this stage whether the method of removing the disturbed layer prior to polishing a silica dust-particle surface is of any importance in determining the nature or extent of formation of the layer produced by polishing. It has already been shown that the nature of the exposed surface of a finely ground silicious dust is determined by the method adopted for removal of the disturbed layer (Part 1B). It was with this result in mind that the subsequent experimental work was undertaken, and its significance is ultimately apparent.

Removal and regeneration of the disturbed layer.

An extractive solubility curve can be plotted for a given material by carrying out a normal solubility test and /

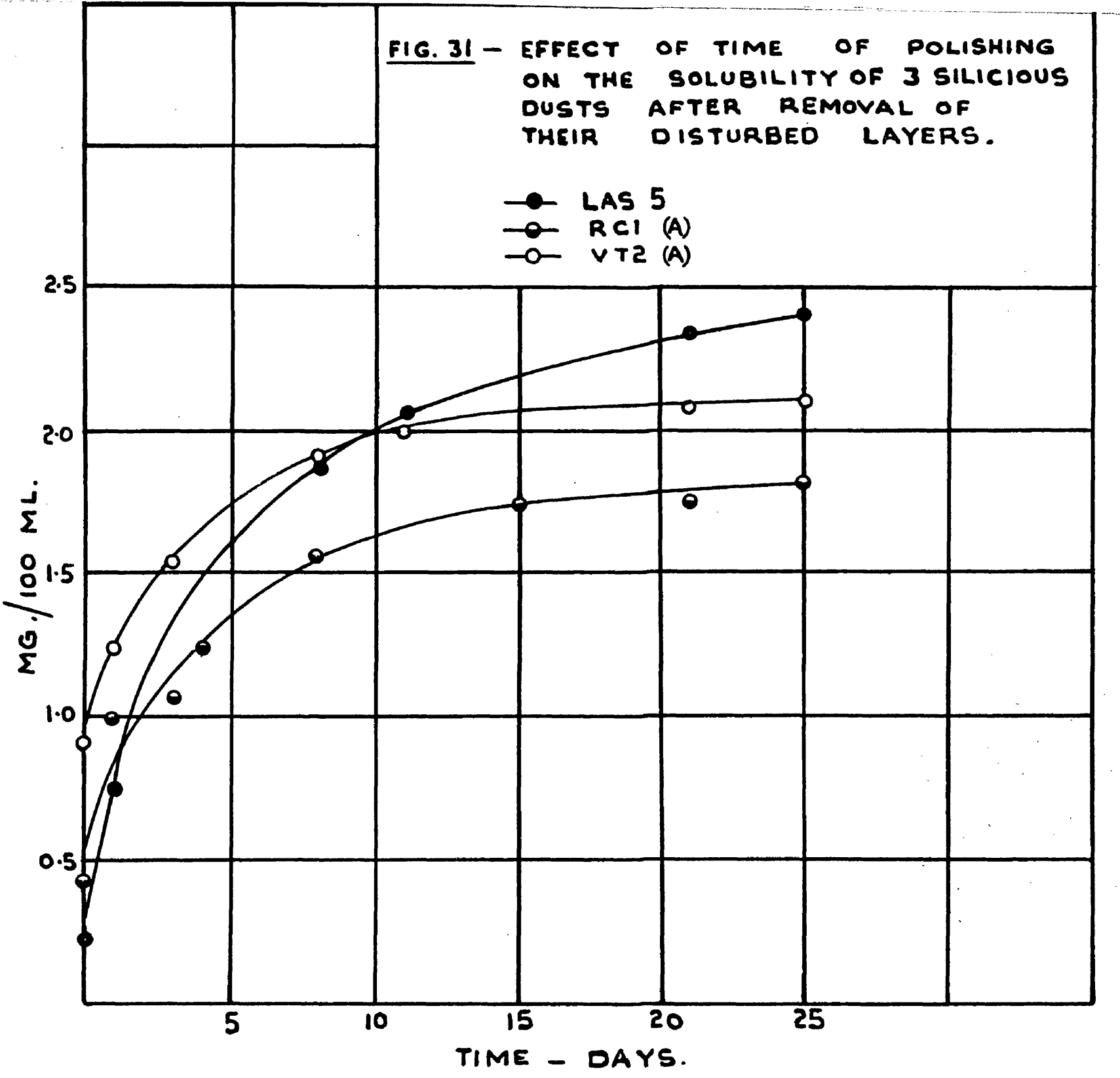
FIG. 31 – EFFECT OF TIME OF POLISHING ON THE SOLUBILITY OF 3 SILICIOUS DUSTS AFTER REMOVAL OF THEIR DISTURBED LAYERS.
LAS 5
RC1 (A)
VT2 (A)
MG./100 ML.
2·5
2·0
1·5
1·0
0·5
5
10
15
20
25
TIME – DAYS.

/by renewing the solvent at the end of each of a number of consecutive solution periods. The solubility after each period is added to the previous value and plotted against time.

Such curves were obtained for duplicate samples of Lochaline-sand (LAS 5) and vitreous silica (VT 2) dusts under the following experimental conditions : mass/liquid ratio for each solution period, 4g./40 ml.; temperature, 37°; pH 7.5. The experiments were interrupted 48 days from the start (i.e. after complete removal of the disturbed layers), and the dusts washed thoroughly with distilled water and dried at 37°.

One 4g. sample of each of the above dusts were polished with 5g. of rock crystal polishing agent in the manner already described. The dusts were separated by repeated sedimentation from distilled water and dried at 37°. The extractive solubility tests were continued and the results are illustrated graphically in Fig. 32.

The initial portions of each curve represent complete dispersion of the disturbed layers on Vitreosil and Lochaline-sand particles. The solubility curve for the polished crys-:talline material is similar in nature to that representing removal of the disturbed layer. The points on this curve immediately after polishing are more frequent than those given by Clelland and Ritchie[55], and the graph therefore indicates a gradual dispersion of the disturbed layer on a polished crystalline substrate. The increases in the rate of solution/

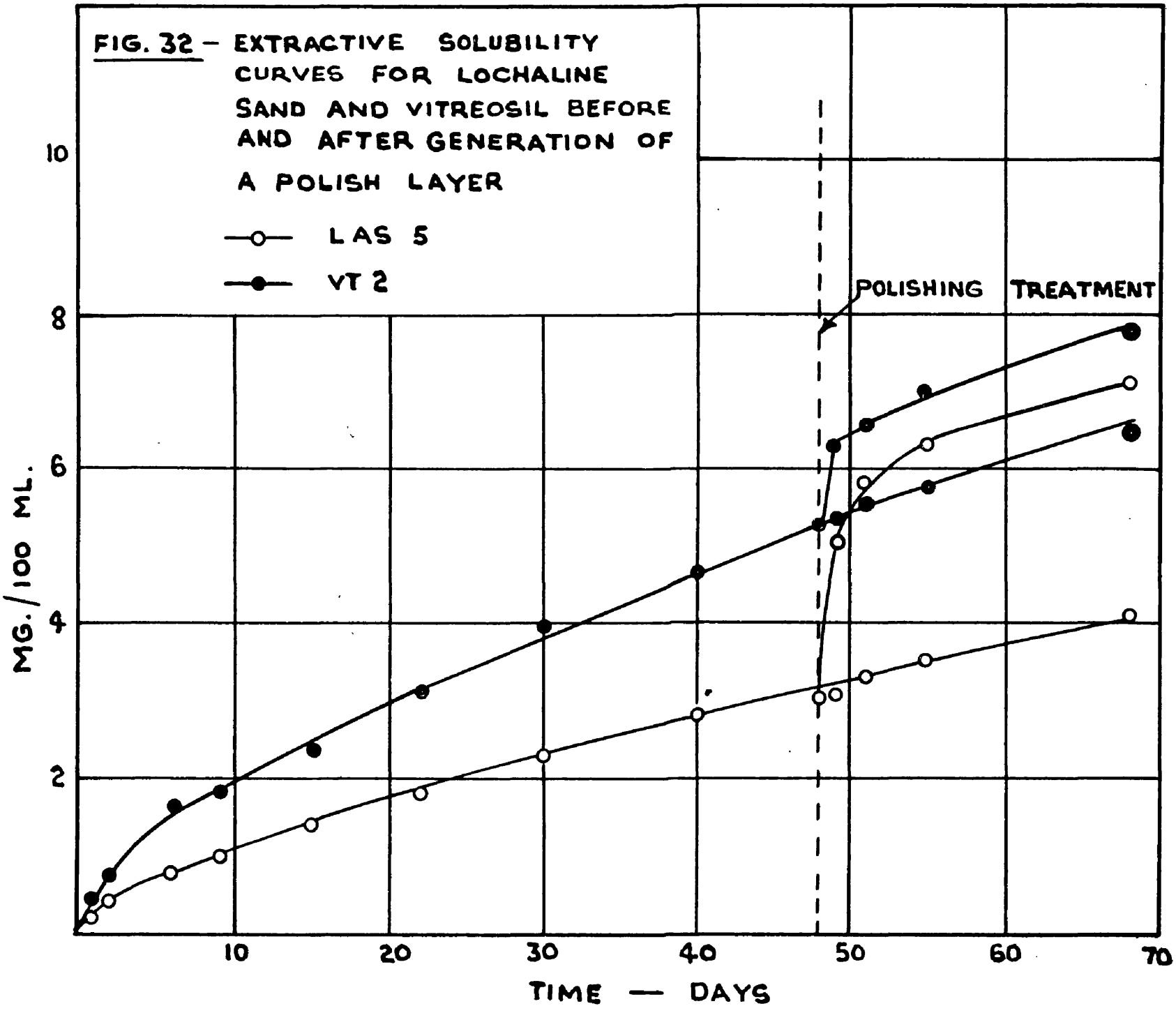
FIG. 32 – EXTRACTIVE SOLUBILITY CURVES FOR LOCHALINE SAND AND VITREOSIL BEFORE AND AFTER GENERATION OF A POLISH LAYER
LAS 5
VT 2
POLISHING TREATMENT
MG./100 ML.
TIME — DAYS
2
4
6
8
10
10
20
30
40
50
60
70

/and solubility are considerable, and approximately the same time of contact of dust and solvent is required to disperse both layers.

Complete dissolution of the regenerated layer on amorphous silica, however, occurs after 24 hours. From this result it may be inferred that the polishing period was not sufficiently prolonged. Fig. 31 shows that a maximum solu-:bility has, in effect, been reached after about 18 days; there must be an alternative explanation for this fast rate of dispersion. The increases in rate of solution and solu-:bility are much smaller than those for crystalline silica, although the polish effect does occur. This increase in solubility would not be expected for wholly amorphous material if the regenerated layer were of the same type of structure as the substrate. This result is analogous to the effect of removal of the disturbed layer from amorphous silica particles on their adsorptive powers (Part 11). There is some evidence[100] for the presence of a crystalline modification in fused 'amor-:phous' silica, which may account for this polish effect.

The electron-diffraction results obtained in Part 1 do not show crystallinity in fused silica either by trans -:mission or reflection of electrons, and it is highly impro-:bable that there are any chemical or structural differences between the core and the disturbed (or regenerated) layers on amorphous silica particles, or between the disturbed and regenerated layers on either crystalline or amorphous silica.

/In view of the methods of production of the two types of surface, one may postulate a physical difference between them. For example, the tenacity with which this regenerated layer is held to the core may be much less than that with which the disturbed layer is held, the former type being consequently more easily dispersed in a solvent. On the other hand, an extension of the concept put forward in Part 11 may also be applicable in this instance. It was postulated that the dis-:turbed layer on Vitreosil particles was of a more open struc-:ture than the core to account for the observed reduction in the affinity of the particles for an adsorbate after removal of the disturbed layer. The surface layer on a polished amorphous silica dust may also have a more open structure than the disturbed layer (again owing to differences in the methods of production), accounting for the observed differences in solution properties.

Effect of the nature of the polished substrate.

As already pointed out, this factor msut also be considered in the light of the foregoing electron-optical examination of the surface structure of finely ground silica. It was shown that removal of the disturbed layer by a borate buffer solution did not affect an underlying transitional layer of cryptocrystalline silica. The presence of this latter layer may account for the gradual dispersion of the regenerated layer of high solubility on the Lochaline sand particles - as is now known to be the cause of the gradual /

/dispersion of the disturbed layer; this would account for the similarity of both halves of the curve for Lochaline sand in Fig. 32. There are no such crystallites present to this extent in fused silica, however, and one would expect the regenerated layer to be more discrete than that on Lochaline-sand particles. It is very probable that the observed solu-:bility phenomena are caused by differences in the structural texture of both types of disturbed layer, and between the layer and the immediate substrate of a crystalline or amor-:phous silica particle.

To investigate further the effect of the presence of these minute crystals on the solution-rate of a polish layer, it was decided to remove the disturbed layer from a quartz sample by two different methods, thereby altering the nature of the substrate, and to compare the solubility curves obtained for disturbed layers generated on the two surfaces by polishing. The methods adopted were as follows :

(a) Prolonged treatment with borate buffer solution, pH 7.5.

(b) Etching with 40% hydrofluoric acid.

The quartz dust produced by method (a) will retain the transitional layer, but will yield the disturbed layer into solution, while both layers will be completely removed by method (b).

Removal of the surface layers.

(a) 5g. quantities of RC 1 were extracted with 40 ml. of borate buffer solution (pH 7.5) in Lusteroid tubes for 24 /

/days at 37°. After thorough washing with distilled water, the material was dried at 37°.

(b) Rock crystal RC 1(A) was used for this part of the experi-:ment, removal of the surface layers from RC 1 by hydrofluoric acid having been effected as described previously.

Polishing Treatment.

10g. of each sample were placed in 2 oz. glass bottles, mixed with 2g. of rock crystal polishing agent, and rotated at 30 r.p.m. for 15 days. The polished dusts were then separated by sedimentation from distilled water and dried at 37°. Microscopic examination of a number of particles of each dust revealed no trace of adherent polishing agent. Extractive solubility tests were carried out (mass/liquid ratio, 4g./40 ml., pH 7.5, temperature 37°) and the results are shown graphically in Fig. 33.

It can be seen from these results that the effect of polishing on the solubility of a silicious dust depends, to some extent, on the degree of crystallinity of the substrate. The equilibrium solubility value exhibited by the quartz sample having the massive core exposed to the action of the polishing agent is greater than that shown by the dust which has retained its transitional layer.

By comparison of these curves with that for polished Vitreosil (Fig. 32), it becomes apparent that the effect of polishing on the equilibrium solubility value of a material with a totally amorphous surface prior to polishing is less

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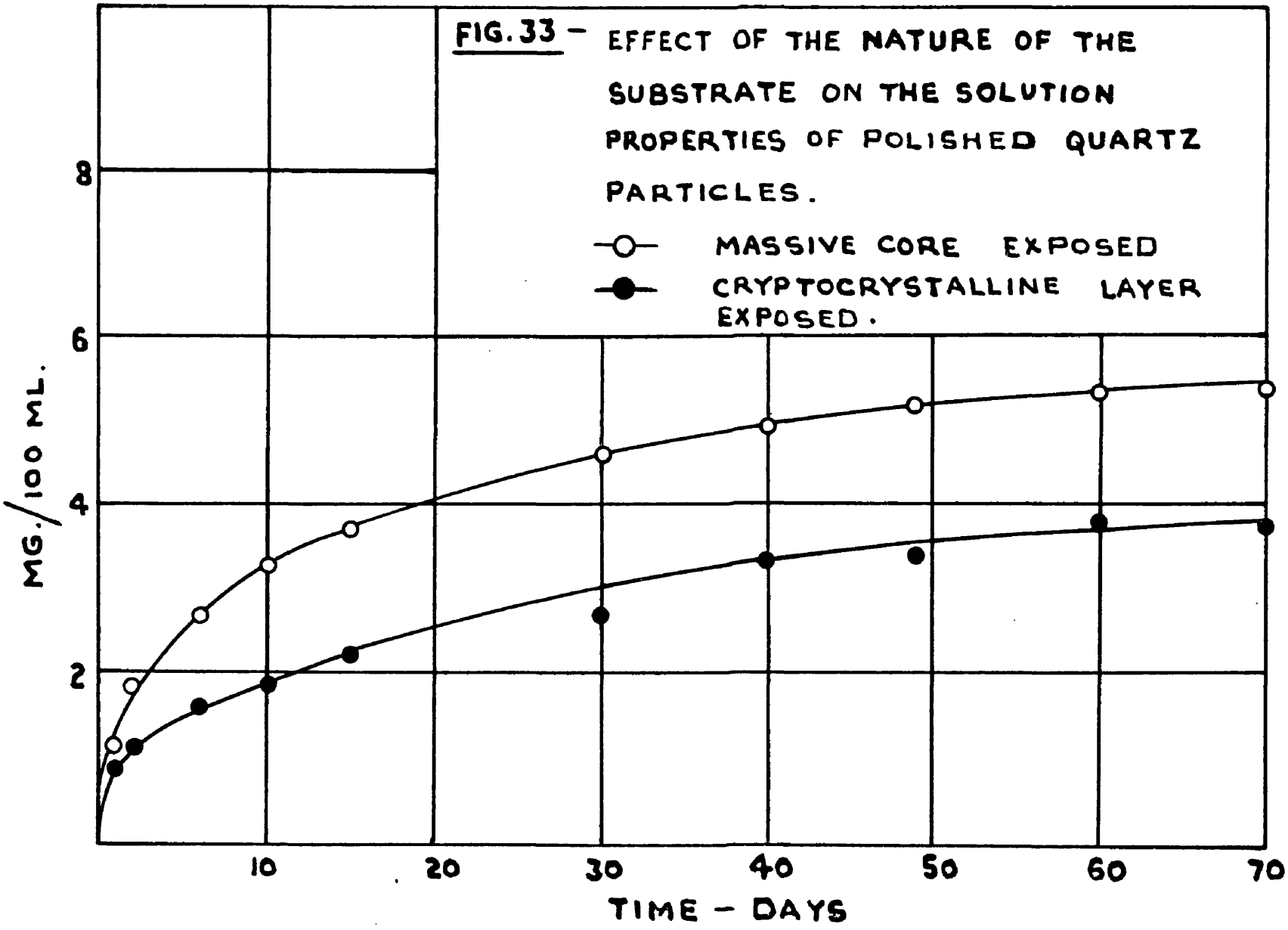
FIG. 33 - EFFECT OF THE NATURE OF THE SUBSTRATE ON THE SOLUTION PROPERTIES OF POLISHED QUARTZ PARTICLES.
MASSIVE CORE EXPOSED
CRYPTOCRYSTALLINE LAYER EXPOSED.
MG./100 ML.
8
6
4
2
10
20
30
40
50
60
70
TIME - DAYS

/than that for a cryptocrystalline surface which, in turn, is less than that for a massive crystalline surface. This effect is probably greater than initially apparent, since the Vitreo-:sil dust was polished for 18 days, while the rock crystal dusts were subjected to 15 days polishing. Thus, under identical polishing conditions, the rate of solution and equi-:librium solubility of a polished silica dust are markedly dependent upon the nature of the surface exposed to the action of the polishing agent.

Effect of polishing on the adsorption of Methylene Blue.

It was shown in Part 11 that the disturbed layers on quartz, Lochaline-sand, and Vitreosil particles had a consider-:ably greater affinity for this basic dyestuff than had the underlying material, indicating that there is some relation-:ship between the solution and sorption properties of such substances, before and after removal of their disturbed layers. Since it is now known that the disturbed layer is comprised of amorphous silica, similar results of adsorption experiments before and after regeneration of a disturbed layer would clearly aid in the establishment of the exact nature of the polish layer. The following adsorption experiments were designed to test this concept.

Preparation of materials. - 20g. each of RC 1(A), LAS 5 (disturbed layer removed) and VT 2(A) were polished for 6 days with 6g. quantities of rock crystal polishing agent. The dusts were separated by repeated sedimentation from distilled /

/water, dried at 120°, and examined microscopically for traces of polishing agent.

To ensure that this treatment had been effective in generating a layer of high solubility on the particle surfaces, the solubilities of the dusts were determined under normal conditions, and the results appear in Table XIII. The poli-:shing process has been effective in generating a layer of high solubility on the particle surfaces.

Adsorption procedure.

The adsorption experiments were carried out as des-:cribed in Part II of the present work and the procedure requires no further explanation. Adsorption curves were obtained for quartz and Vitreosil (using 1g. quantities) and for Lochaline sand (using 0.25g. quantities) before and after polishing, and are shown in Fig. 34.

Solution and sorption properties of the three sili-:cious dusts tested are markedly enhanced by the production of a disturbed layer on the particle surfaces. The affinity of the particles for the adsorbate has markedly increased in each case, a parallel result to that obtained on removal of the disturbed layers from similar surfaces produced by grinding. From these considerations it would seem that the disturbed layer and the regenerated layer are virtually identical.

Since Vitreosil is completely amorphous it provides an anomalous result - as did the removal of the disturbed layer from a ground vitreous silica surface. The decrease in equi-

/

TABLE XIII.

Effect of polishing for 6 days on the solubilities of quartz, Lochaline sand and Vitreosil (disturbed layers previously removed).

Solubilities are expressed as mg./100 ml. after 72 hours in borate buffer (pH 7.5) at 37°; mass/liquid ratio 4g./40 ml.

Sample		mg./100 ml.
Quartz	: Before polishing	0.58
	After polishing	1.54
Lochaline sand	: Before polishing	0.27
	After polishing	1.13
Vitreosil	: Before polishing	0.92
	After polishing	2.82

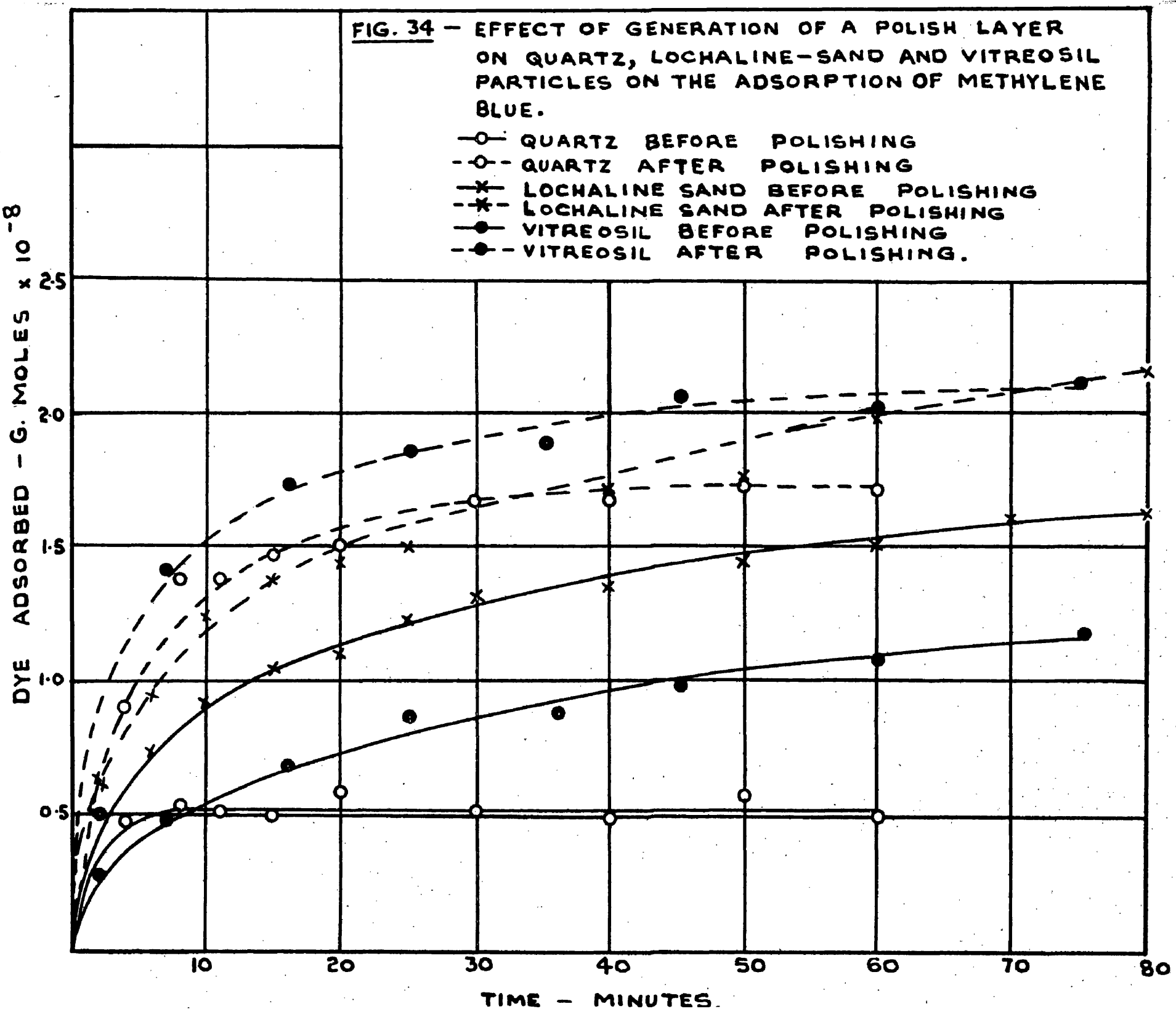
FIG. 34 – EFFECT OF GENERATION OF A POLISH LAYER ON QUARTZ, LOCHALINE–SAND AND VITREOSIL PARTICLES ON THE ADSORPTION OF METHYLENE BLUE.
QUARTZ BEFORE POLISHING
QUARTZ AFTER POLISHING
LOCHALINE SAND BEFORE POLISHING
LOCHALINE SAND AFTER POLISHING
VITREOSIL BEFORE POLISHING
VITREOSIL AFTER POLISHING.
DYE ADSORBED – G. MOLES x 10⁻⁸
2·5
2·0
1·5
1·0
0·5
10
20
30
40
50
60
70
80
TIME – MINUTES.

/:librium adsorption on removal of the disturbed layer, however, is not as large as the increase in equilibrium adsorption attributable to the presence of the regenerated layer. This may again be accounted for by assuming the layer on a polished Vitreosil surface to have a more open structure than its counterpart, the disturbed layer produced by grinding, ren-:dering the former the more chemically and physically active.

/Electron-optical examination of polished silica surfaces.

In recent years the technique of electron diffraction has proved very useful for the examination of the structure of the layer formed by the polishing of certain surfaces, and it was decided to adopt this method to continue the present investi-:gation of the effect of polishing on the surface structure of silicious dust particles. The formation of an amorphous surface-layer would be expected to obscure diffraction effects at a crystalline silica surface at high accelerating voltages, and possibly obliterate such effects at lower (less penetrating) voltages. The following experiments were designed to provide further evidence for the close similarity which, from the pre-:vious chemical investigations, is now apparent between the disturbed layer produced on silica surfaces by crushing and grinding operations, and the disturbed layer produced by agitation with an abrasive.

The particle sizes of the dusts which have been used in the previous experiments are, of course, too large to be of much use in the transmission-type electron microscope. It was first thought that the use of a sufficiently finely divided silica would present some difficulty during the polishing process because of the large surface area to be polished. Such problems did not arise, however, since initial experiments showed that a reversal of the procedure adopted in the previous polishing experiments is suitable for use in electron-optical studies of the surface layer produced by polishing. While it /

/is known that agitation of an etched quartz dust (having a particle size of, say, 300μ) with finely ground quartz generates a disturbed layer of high solubility on the particle surfaces, it seemed possible that large quartz particles would generate a similar layer on finely ground, etched, silica dusts during polishing. This was confirmed by simple experi-:ment, and since it proved very effective, the method was used in the present work. It is highly probable that self-abrasion of the finely ground silica is, to a large extent, responsible in generating a disturbed layer, while the polish-:ing agent has a low specific surface and less effective abrasive properties.

Materials : source and preparation of dusts.

Quartz. - Selected crystals of Madagascar quartz were ground in a Christy-Norris hammer-mill, using a $\frac{1}{4}$ in. screen. The 50 - 70 - mesh fraction of the sieved material was extrac-:ted with concentrated hydrochloric acid to remove iron con-:tamination, washed thoroughly with distilled water, and dried at 100°. This sample was ground for 6 hours in a mechanical agate mortar.

Removal of the disturbed layer.

The above sample was extracted with 40% hydrofluoric acid (A.R.) for five minutes in a polythene beaker. The sus-:pension was diluted and filtered through four thicknesses of filter paper, washed thoroughly with distilled water to remove traces of acid, and dried at 120°.

/Polishing treatment.

The polishing agent used was a 50 - 70 - mesh sample of Madagascar quartz, purified by hydrochloric acid extraction. The sample was washed thoroughly and dried at 100°.

20g. of finely ground, etched quartz prepared as above was mixed with 40g. of polishing agent in a 4 oz. glass bottle closed with a screw-cap lid and the whole rotated at 30 r.p.m. for 20 days. This large quantity of polishing agent was required to prevent adhesion of the fine material to the sides of the glass container by electrostatic forces. The materials were separated by repeated sedimentation of the polishing agent from distilled water and filtration of the water suspension of the polished material through two thick-:nesses of filter paper; the dust was dried overnight at 120°.

Solubility of the dusts.

To ensure that the foregoing etching and polishing treatments had effectively removed and regenerated highly soluble layers on the dust particles, the solubility of each dust in borate buffer was determined before and after etching, and after polishing. Separation of solid and liquid phases was effected by centrifugation as in previous experiments. The results (Table XlV (A)) indicate that the treatments have resulted in the removal and regeneration of highly soluble sur-:face layers.

Electron-optical examination of samples.

Samples before and after polishing were prepared for /

TABLE XlV (A)

Solubility of quartz in borate buffer (pH 7.5) after 48 hours at 37°; mass/liquid ratio, 0.2g./40 ml.

Sample	mg./100 ml.
Untreated	3.60
Etched	0.13
Polished	0.50

/the electron microscope by dispersing in pure n-butyl alcohol and spraying from an atomiser on to a gently heated collodion-covered specimen grid. Some of the samples were shadow-cast with gold-palladium, at $\cot^{-1} 2$.

Examination of quartz.

Typical electron-micrographs of the samples before and after polishing are shown in Figs. 35, 36 and 37. The micrographs taken before polishing, of which Fig. 35 is typical, show clearly defined crystal faces; electron-diffraction pat-:terns of the two samples were recorded by the transmission method using 60-kV electrons (Figs. 38 and 39 respectively).

The sample before polishing indicates a considerable degree of crystallinity and the polishing process has resulted in the production of less distinct spots, pointing to a lesser degree, or even complete absence, of crystallinity in the sur-:face layers of the polished sample. The crystallinity yet apparent in the polished dust (Fig. 39) is probably due to the penetration of electrons at this high accelerating voltage through the thin surface layers with subsequent diffraction at the substrate. This difference in diffraction patterns was observed previously before and after removal of the disturbed layer from finely ground quartz particles (Figs. 3 and 4). There is thus some physical evidence for the similarity already observed between the layer produced by polishing, on the one hand, and grinding, on the other.

The effect of the polishing process on the surface

/

/structure of the particles becomes more apparent at lower accelerating voltages. Diffraction patterns from the two samples were observed at 20 kV., and Fig. 40 shows that dif-:fraction spots were again evident in the patterns produced by the sample before polishing. The patterns obtained from the sample after polishing showed only collodion bands, and indi-:cated no crystallinity (Fig. 41).

It appears, therefore, that the layers near the sur-:faces of polished quartz particles are amorphous (similar to the structure of the disturbed layer produced by grinding, which has already been discussed). This is probably an effect similar to that observed by Kamokawa[101] on the surface of polished quartz. Comparison of the electron micrographs taken before polishing (Fig. 35) and after polishing (Figs. 36 and 37) indicates an apparent increase in the size of the par-:ticles - an effect which cannot be accounted for in terms of the above surface changes. This effect, however, may be caused by a breaking up of the large particles of rock crystal polishing agent. If this occurs to an appreciable extent, the assumption that the diffraction effects apparent in Fig. 39 may be due to penetration of a fair proportion of 60-kV. electrons through the surface-layers is not completely justi-:fied. Diffraction may also occur at the surfaces of abraded quartz particles. To distinguish between diffraction effects produced by the ground quartz itself and those produced by quartz particles broken off from the polishing agent is /

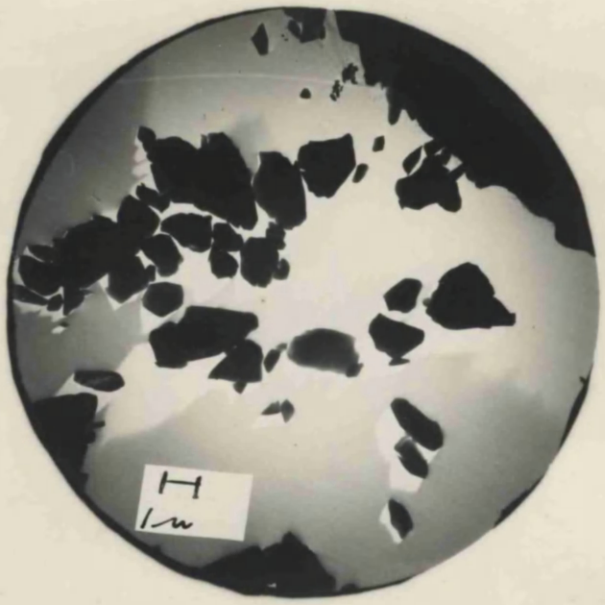

FIG.35. Micrograph of etched quartz before polishing. Shadow-cast with gold-palladium at $\cot^{-1} 2$ (X 3000)

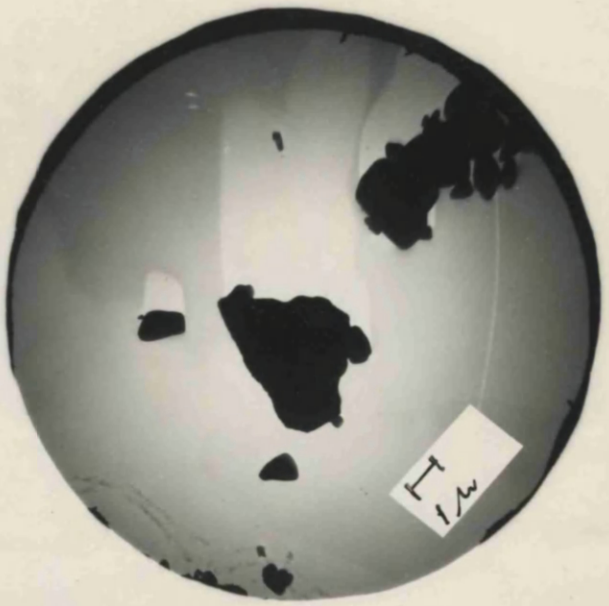

FIG.36. Micrograph of etched quartz after pol-:ishing. Shadow-cast with gold-palladium at $\cot^{-1} 2$ (X 3000)

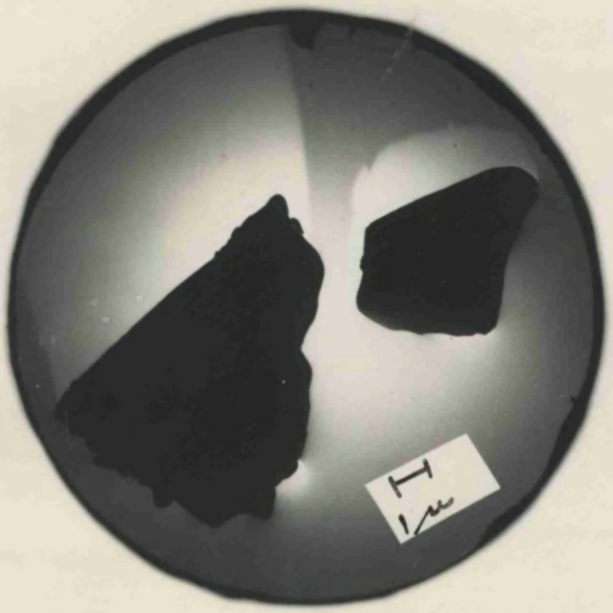

FIG.37. Micrograph of etched quartz after polishing. Shadow-cast with gold-:palladium at $\cot^{-1} 2$ (X 3000)

FIG.38. Diffraction pattern of etched quartz before poli-:shing. Transmission method, with 60-kV. electrons

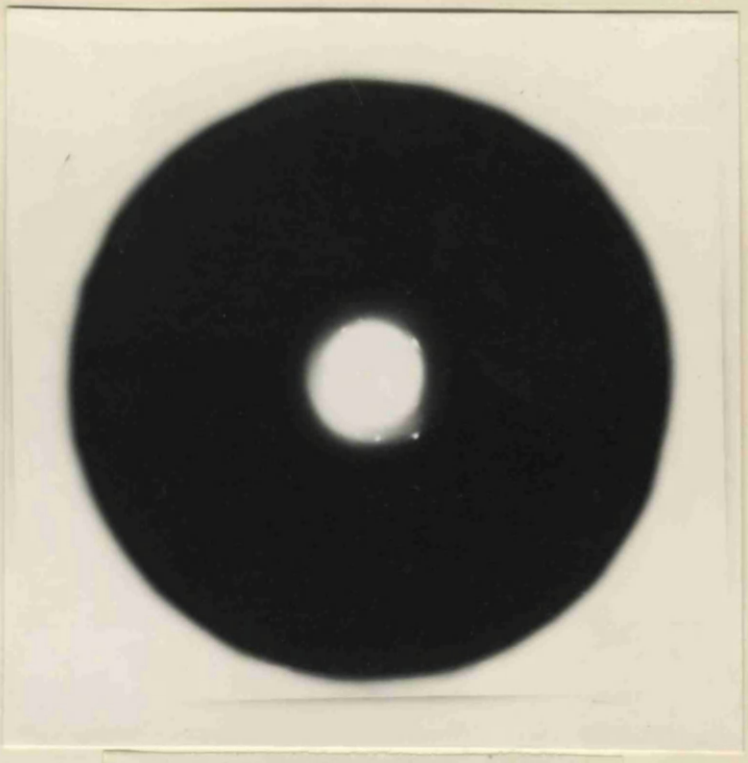

FIG.39. Diffraction pattern of etched quartz after poli-:shing. Transmission method, with 60-kV. electrons

FIG.40. Diffraction pattern of etched quartz before poli-:shing. Transmission method, with 20-kV. electrons

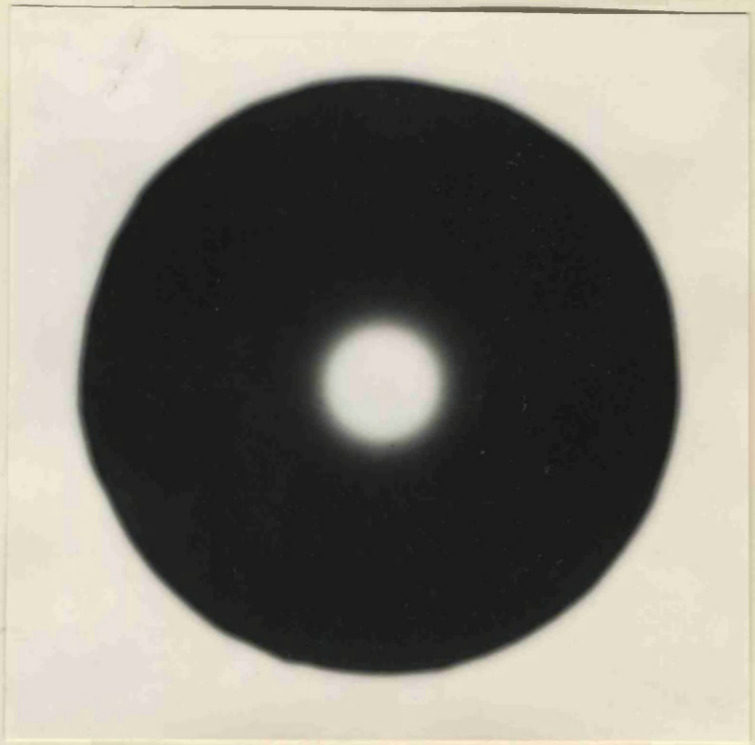

FIG.41. Diffraction pattern of etched quartz after poli-:shing. Transmission method, with 20-kV. electrons

/impossible on the evidence so far obtained. In order to make such a distinction, and to investigate whether the effect takes place on any appreciable scale, it was decided to polish a sample of amorphous silica with rock crystal polishing agent. In this case abraded particles of polishing agent would be easily distinguished by their ability to diffract electrons.

Examination of Vitreosil.

A sample of transparent Vitreosil was prepared exactly as for quartz and etched with 40% hydrofluoric acid (A.R.). The material was polished for 30 days with the polishing agent used in the quartz experiment and the solu-:bilities of the dusts in borate buffer are shown in Table XlV (B). Again the treatments have resulted in the removal and regeneration of highly soluble surface layers. The materials were prepared as before for examination in the electron microscope.

Typical electron-micrographs, taken before and after regeneration of the disturbed layer, are shown in Figs. 42, 43 and 44. This material is normally assumed to be wholly amorphous and removal of the disturbed layer produces no change in the diffraction pattern of ground Vitreosil (Part 1 B). It was thus expected that the above polishing process would produce no change in the diffraction pattern of etched Vitreo-:sil. Fig. 45 is a representative diffraction pattern of the sample before polishing, recorded at 60 kV. On the whole, diffraction patterns remained unchanged after polishing, but

/

TABLE XlV (B)

Solubility of Vitreosil in borate buffer (pH 7.5) after 48 hours at 37°; mass/liquid ratio 0.2g./40 ml.

Sample	mg./100 ml.
Untreated	6.72
Etched	0.78
Polished	1.42

/an apparent increase in particle size was again observed.

Diffraction patterns were obtained from the polished material, but were not representative. Figs. 46 and 47 were obtained with 60-kV. electrons and are clearly due to particles of Madagascar quartz which had become detached from the polishing agent. The central rhombohedral particle in Fig.44, for example is responsible for the diffraction spots in Fig.47 indicating that the particle is crystalline. Such particles were very rare, however, and it is concluded that the effect does not occur to any appreciable extent. Furthermore, the solubility changes are truly an effect of polishing and not of fragmentation of particles of polishing agent. The apparent increase in particle size may be due to this minor effect or, possibly, to agregation during polishing. It is considered, however, that agregates of this nature would be completely dispersed during specimen preparation.

RECRYSTALLISATION OF AN AMORPHOUS SURFACE LAYER.

It has been shown[57] that although the disturbed sur-:face layer on finely ground quartz particles prevents the true silica content of the dust from being determined by differential thermal analysis, prior removal of this non-quartz layer by etching eliminates this disability. Since Finch[102,103] has claimed, on the basis of electron-optical studies, that an amorphous layer on the polished crystal faces of certain materials in massive crystalline form (e.g. calcite) can be recrystallised by heating, it is reasonable to enquire whether /

FIG.42. Micrograph of etched Vitreosil before polishing. Shadow-cast with gold-palladium at cot-1 2 (X 3000)

FIG.43. Micrograph of etched Vitreosil after polishing (X 3000)

FIG.44. Micrograph of etched Vitreosil after polishing (X 3000)

FIG.45. Diffraction pattern of etched Vitreosil before polishing. Trans-:mission method, with 60kV. electrons

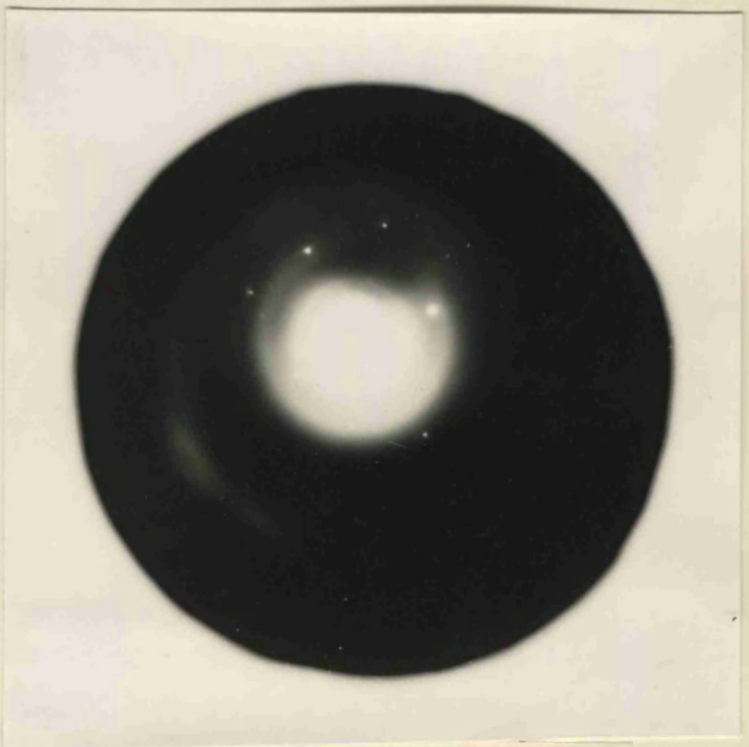

FIG.46. Diffraction pattern of etched Vitreosil after polishing. Trans-:mission method, with 60-kV. elect-:rons

FIG.47. Diffraction pattern of etched Vitreosil after polishing. Trans-:mission method, with 60-kV. elect-:rons

/finely ground quartz dusts could be adequately prepared for differential thermal analysis by prior heat treatment. There is, it is true, evidence[93,104] that the annealing of vitreous silica in bulk is too slow for effective utilisation. This may not be so, however, for extremely thin surface layers; there is some evidence that vitreous silica may develop a thin surface-crystallinity on repeated heating to about 750° - 950°, for Barrer[53] has observed that the permeability of vitreous silica by gases, such as air, nitrogen and argon, if measured repeatedly at temperatures in this neighbourhood, decreases progressively but is restored to its original value when the silica surface is etched by hydrofluoric acid. He attributes the decrease in permeability to 'crystalline develop-:ments in the surface layers', and its restoration to exposure of the vitreous surface once again by etching.

To provide further evidence for the amorphous nature of the disturbed layer on polished quartz particles, thermal recrystallisation has been attempted with some measure of success. The possibility of thermal recrystallisation of the disturbed layers produced on quartz and vitreous silica dusts by grinding has also been investigated.

EXPERIMENTAL.

Materials ; source and preparation of dusts.

Quartz. - Madagascar quartz crystals were selected for purity and ground in a Christy-Norris hammer-mill using a ¼ in. screen, and the 50 - 70 - mesh fraction of the sieved material /

/was purified by treatment with concentrated hydrochloric acid. After thorough washing with distilled water and drying at 100°, the material was etched with 40% hydrofluoric acid (A.R.), washed thoroughly and dried at 110° to give dust RC 2(A).

Quartz and fused silica for electron-optical examination. -

These materials were portions of the samples pre-:pared as described on pages 94,98, and the finely ground, etched, polished quartz and finely ground, untreated Vitreosil samples were used.

Effect of heat on the solubility of a polished dust.

If it is possible to recrystallise an amorphous sur-:face layer on silicious dust particles by thermal treatment, then it is reasonable to predict a gradual decrease in the solubility of a silica dust carrying such a layer if subjected to increasing temperatures. To investigate this possibility, 40g. of etched quartz, RC 2(A), were polished in the normal way with finely ground rock crystal polishing agent for 34 days. The dusts were separated by sedimentation from distilled water and the polished quartz dried at 37°. Microscopic examination showed that the dust was completely free from traces of polishing agent.

4g. samples of the polished material were weighed into an alumina combustion boat and heated in a mullite com-:bustion tube in an electric furnace, the temperature being thermostatically controlled and measured by a chromel-alumel thermocouple. After heating samples at various temperatures /

/for 17 hours their solubilities in borate buffer solution were determined, the results being shown in Table XV. From these it will be seen that it is possible to reduce the solubility of a polished quartz dust by heating at temperatures between about 600° and 1200°; thermal recrystallisation of the sur-:face layers may account for the solubility/temperature effect. The latter temperature is insufficient to effect complete reduction to the value observed prior to production of the polish layer. That this change is due to the effect of ther-:mal treatment on a surface different from the substrate, and not to any other factor, can be seen by comparison of the fore-:going results with those in Table Vll (Part ll), which show the effect of heat treatment on an untreated crystalline silica surface. Although the disturbed layer is present on these Lochaline-sand particles it is undoubtedly very thin, since the particle size of the sample is of the order 125μ, and heat treatment at 1000° has not altered the solution pro-:perties, even after 24 hours at this temperature. This effect on the solubility of a polished quartz dust (on which the dis-:turbed layer is at maximum thickness) might possibly be ascribed to partial recrystallisation of the layer. It is also a result which substantiates the previous conclusion that the layer produced by polishing is amorphous in nature, like the disturbed layer produced by grinding, since the solubility decreases with increasing pre-treatment temperature and the solubility of crystalline silica is less than that of fused /

TABLE XV.

Effect of heat treatment on the solubility of a polished quartz dust.

Solubilities of polished RC 2(A) in borate buffer (pH 7.5) after 48 hours at 37°; mass/liquid ratio, 4g./40 ml.

Temperature of heat treatment	mg./100 ml.
Before treatment	1.51
580°	1.40
805°	1.18
935°	1.10
995°	1.04
1145°	0.94
1190°	0.89
Solubility before polishing	0.49

/silica under the same conditions. The result is in accordance with the picture of the disturbed layer which has emerged from previous considerations.

Electron-optical examination of samples.

Heat Treatment. - Samples of finely ground, etched, polished quartz dust and finely ground untreated Vitreosil were heated at 925° for 18 hours, cooled for one hour, and heated again at 925° for four hours. The specimens were allowed to cool in the furnace.

Solubility of the dusts.

To ensure that the effect of heat on these samples was similar to that already observed, their solubilities in borate buffer were determined under normal conditions and the results are quoted in Table XVl. It can be seen that thermal treatment has reduced the solubilities of the polished quartz dust as before, and also of the finely ground amorphous silica. In order to correlate this data with changes in surface struc-:ture, the following electron-optical examination was carried out.

Preparation of samples.

Specimens were prepared for the electron microscope and the electron-diffraction camera by methods already described in Part 1B.

Examination of Vitreosil.

Typical electron micrographs taken before and after heating showed no change in the nature or size of the particles.

/

TABLE XVl.

Solubility of quartz and Vitreosil in borate buffer (pH 7.5) after 48 hours at 37°; mass/liquid ratio, 0.2g./40 ml.

	Sample	mg./100 ml.
Quartz :	After polishing	0.50
	Polished sample after heating	0.32
Vitreosil :	Untreated	6.72
	After heating	1.15

Electron-diffraction patterns of the sample before heating (Fig. 45) and after heating (Figs. 48,49 and 50) were recorded by the transmission method using 60-kV. electrons. It appears from these diffraction patterns that thermal treatment has produced signs of recrystallisation in the surface layers of the particles. Diffraction patterns for this material were originally wholly amorphous, showing only collodion bands (Fig. 45, for etched Vitreosil), now a line, and in some cases a spot pattern has been obtained. Only a small proportion of the particles, however, exhibited any degree of crystallinity.

Examination of quartz.

Diffraction patterns have already been observed for polished quartz before heating, at accelerating voltages of 60 kV. and 20 kV. (Figs. 39 and 41 respectively), and were now recorded after heat treatment, at 60 kV. and 20 kV. (Figs. 51 and 52 respectively). Even at 60 kV. the pattern has become less diffuse after thermal treatment, but on the basis of the photographs at 20 kV. (Figs. 41 and 52) it is apparent that the surface layers of polished quartz have undergone to some extent, the process of devitrification, since the heated sample shows a spot pattern and the surface layers of the sample are completely amorphous before heating.

The above specimens of polished quartz and Vitreosil, after heating, were examined in the electron-diffraction camera by the reflection method, at 75 and 50 kV. Typical patterns

/photographed at these voltages indicate no pronounced crys-:tallinity in the sample of Vitreosil, while for the polished quartz a spot pattern is obtained at both voltages (Figs. 53 and 54). This would be expected, however, since electrons at these potentials would penetrate the disturbed layer a few hundred Å. units in thickness to be diffracted at the core. The reduced number of spots at 50 kV., however, would seem to indicate a certain amount of change in the surface layers. These results apparently contradict those obtained with the transmission method and indicate that no substantial recrys-:tallisation has occurred. They must be interpreted with caution because of the depth of penetration of 50 and 70-kV. electrons. An accelerating voltage of 25 kV. would have been very suitable for this examination but the particle size of the dust was apparently too large (after 6 hours grinding), and charging of the particles in the electron beam made it impossible for the specimen to be examined at this low voltage. On the basis of the results at 50 and 75 kV., however, it is apparent that the polishing process does not regenerate a tran-:sitional layer (previously removed by etching) since no con-:tinuous diffraction rings were observed.

The fact that the reflection technique did not detect crystallinity in the sample of Vitreosil after heating may be explained as follows. With this method, the electron probe is large and a statistical number of particles is examined in

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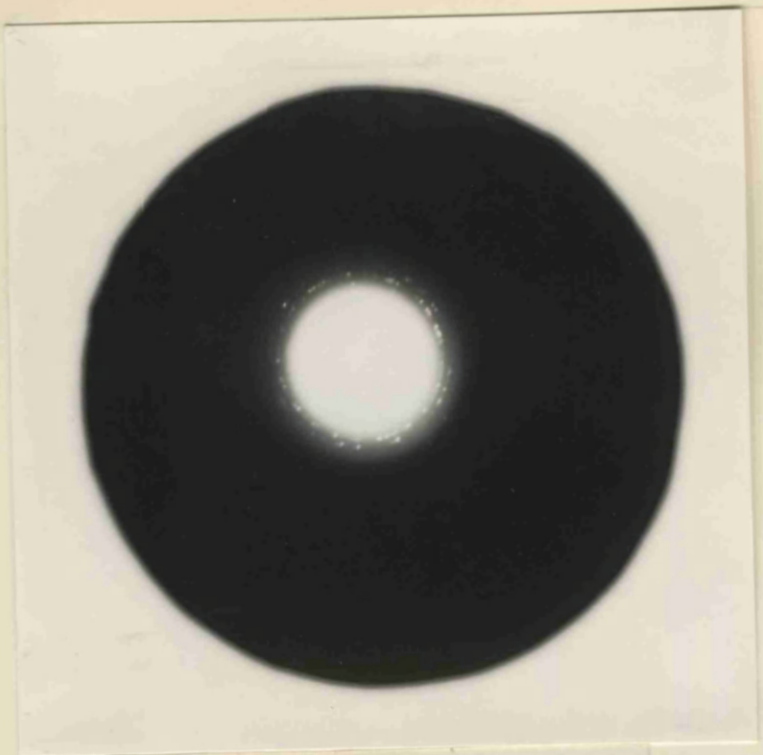

FIG.48. Diffraction pattern of Vitreosil after heat treatment. Transmission method, with 60-kV. electrons

FIG.49. Diffraction pattern of Vitreosil after heat treatment. Transmission method, with 60-kV. electrons

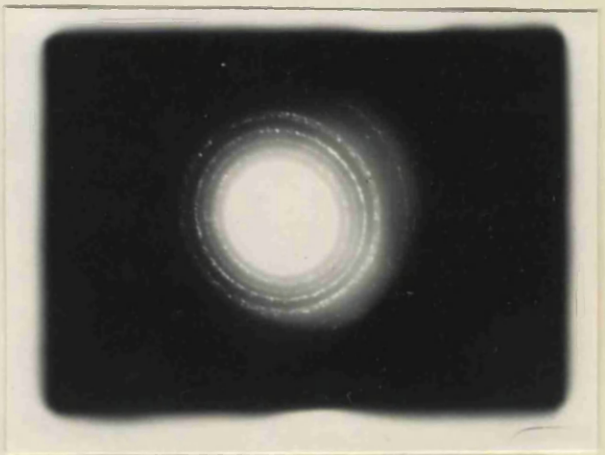

FIG.50. Diffraction pattern of Vitreosil after heat treatment. Transmission method, with 60-kV. electrons

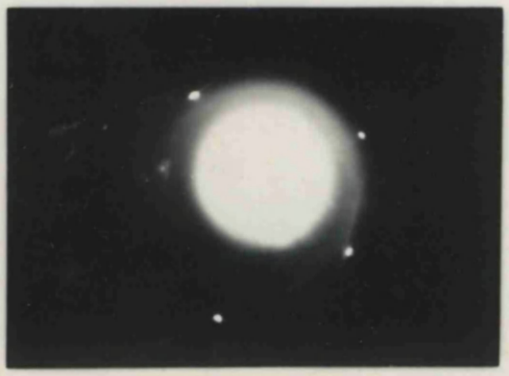

FIG.51. Diffraction pattern of polished quartz after heat treatment. Trans-:mission method, with 60-kV. elect-:rons

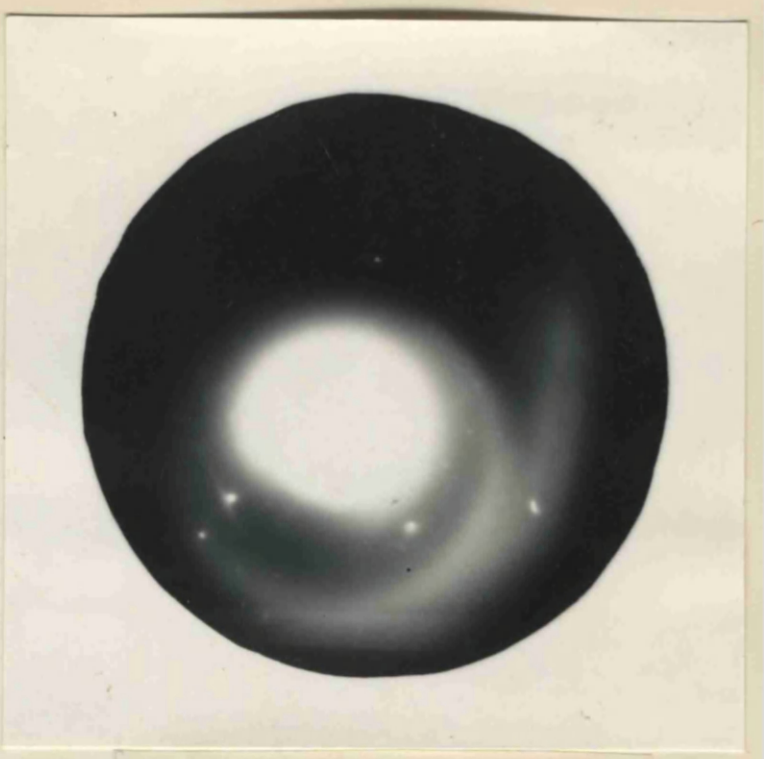

FIG.52. Diffraction pattern of polished quartz after heat treatment. Trans-:mission method, with 20-kV. elect-:rons

FIG.53. Diffraction pattern of polished quartz after heat treatment. Reflec-:tion method, with 75-kV. electrons

FIG.54. Diffraction pattern of polished quartz after heat treatment. Reflec-:tion method, with 50-kV. electrons

/the beam; any diffraction occurring from a few particles may have been masked by amorphous haloes and the diffuse nature of the pattern produced by the bulk of the material.

To investigate this possibility, a fresh sample of Vitreosil was prepared and the specimen subjected to heat treatment before examination by transmission and reflection of electrons.

Confirmation by the transmission method.

In order to minimise charging-up difficulties the sample of finely ground Vitreosil was prepared with a much smaller particle size. Preparation was as before, but in this experiment, the 50 - 70 - mesh sample of transparent Vitreosil was ground for 22 hours, instead of 6 hours as before. The thermal treatment was also more severe in order to increase the extent of apparent devitrification.

2g. of finely ground Vitreosil were heated for 21 hours at 1062° and allowed to cool in the furnace to 165°. The sample was again heated to 985° for 22 hours and cooled to room temperature; a third period of heating was for 24 hours at 1045°, the sample being cooled in the furnace as before. The solubility of the dust was determined before and after heating under conditions of solution identical with those in Table XVl. The solubility of the material was reduced from 8.2 mg./100 ml. to 0.86 mg./100 ml. by thermal treatment. The particle size of the new sample is smaller than that of the previous specimen since the former solubility value (8.2 mg./

/100 ml.) is higher than that for the untreated Vitreosil in XVl.

Examination of samples.

Diffraction patterns of the thermally treated amor-:phous silica were recorded by the transmission method at 60 kV. and are shown in Figs. 55 and 56. It can be seen once again that heating produces a recrystallisation in the surface layers of the particles. Crystallinity was apparent to a greater extent than previously since a fair proportion of the particles on the grid were capable of diffracting electrons. Fig. 56 shows a cross-grating pattern from a very small perfect crystal of silica.

The specimen was examined in the diffraction camera at 75-kV. and a representative pattern shows the near-amorphous state of the Vitreosil, but there are a few spots, more apparent on the negative than on the print, which seem to indicate crys-:tallinity of a few particles (Fig. 57).

Recrystallisation of the disturbed layer on finely ground quartz particles.

From the foregoing results it would seem that the number of particles of polished quartz or untreated Vitreosil whose surfaces have undergone structural change is not very great and hence the thermal treatment, as it stands, does not render a sample of vitreous silica or polished quartz capable of being estimated for silica content by differential thermal analysis. The results with polished quartz are possibly an /

FIG.55. Diffraction pattern of Vitreosil after heat treatment. Transmission method, with 60-kV. electrons

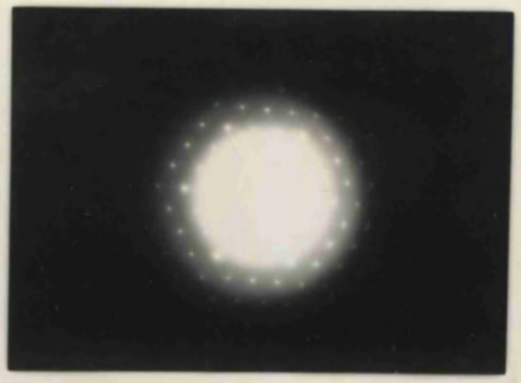

FIG.56. Diffraction pattern of Vitreosil after heat treatment. Transmission method, with 60-kV. electrons

FIG.57. Diffraction pattern of Vitreosil after heat treatment. Reflection method, with 75-kV. electrons

/indication of the extent of recrystallisation to be expected within the disturbed layer on ground quartz particles.

A sample of pure quartz was prepared by crushing selected Madagascar crystals in a Christy-Norris hammer-mill using a $\frac{1}{4}$ in. screen and purifying the 70- 90- mesh fraction with concentrated hydrochloric acid. The washed and dried material was ground for 24 hours in a mechanical agate mortar.

Heat treatment of sample.

A portion of the material prepared as above was heated to 1095° for 24 hours and cooled to 385°, heated to the same temperature for a further 24 hours and cooled to atmospheric temperature. It was finally heated to 1135° for 30 hours and cooled to atmospheric temperature.

The solubilities of the dusts before and after heating were determined in borate buffer solution (pH 7.5) after 48 hours at 37°, mass/liquid ratio 0.2g./40 ml. The solubility was found to be reduced from 8.0 mg./100 ml. to 0.60 mg./100 ml. by the thermal treatment.

Electron-optical examination of samples.

Samples before and after heating were prepared for the electron-diffraction camera as before, and examined by the reflection method.

Diffraction patterns were recorded at 75 kV. before and after heating, and representative plates are shown in Figs. 58 and 59. It can be seen that the two samples give substantially the same pattern, i.e. sharply defined spotted /

/rings. At 50 kV. (Figs. 60 and 61) the number of spots is rather less for both samples and even less so in the pattern from the sample before heating (Fig. 60). At 25 kV. (Figs. 62 and 63) there is a small number of spots from the thermally-treated sample, but no spots from the original specimen. On the whole, therefore, there is definite evidence of some recrystallisation of the surface layers after severe heat treatment.

CONCLUSIONS.

1. A disturbed layer of maximum thickness is generated on silica dust particles (Lochaline sand, rock crystal and Vitreo-:sil) after 15 days polishing with a fine rock crystal abrasive, under the experimental conditions described.

2. Dispersion of a disturbed layer on a polished crystalline silica substrate is a gradual process, while the layer on vitreous silica is dispersed in solution after 24 hours contact. It is apparent from extractive solubility results for disper-:sion of both types of disturbed layer that approximately the same time of contact of dust and solvent is required to dis-:perse both layers on a crystalline surface. It is postulated that the disturbed layers, produced by crushing and grinding silica particles, are virtually identical in structure, dif-:ferences in methods of production being responsible for minor physical differences in the layers. The disturbed layer on polished amorphous silica may exhibit different solution pro-:perties from the disturbed layer on ground amorphous silica /

FIG.58. Diffraction pattern of quartz before heat treat-:ment. Reflection method, with 75-kV. electrons

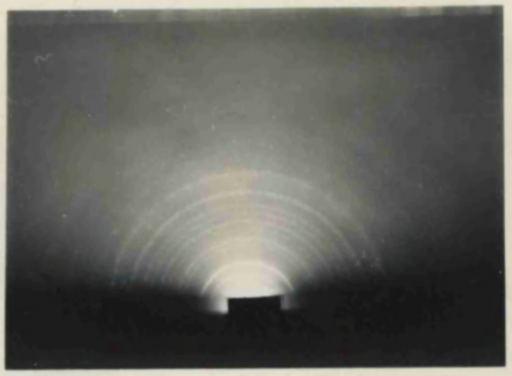

FIG.59. Diffraction pattern of quartz after heat treat-:ment. Reflection method, with 75 kV. electrons

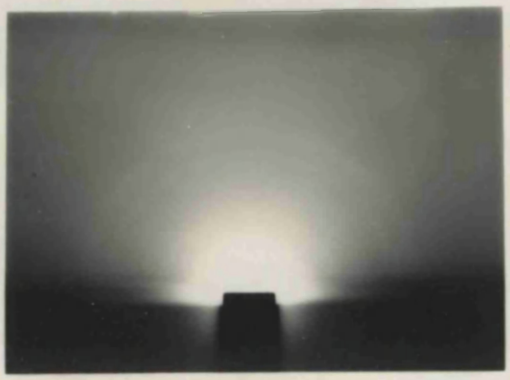

FIG.60. Diffraction pattern of quartz before heat treat-:ment. Reflection method, with 50-kV. electrons

FIG.61. Diffraction pattern of quartz after heat treat-:ment. Reflection method, with 50-kV. electrons

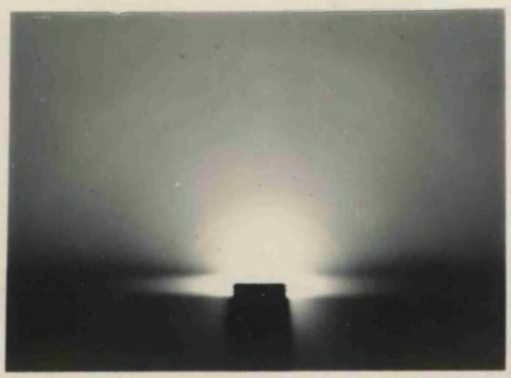

FIG.62. Diffraction pattern of quartz before heat treat-:ment. Reflection method, with 25-kV. electrons

FIG.63. Diffraction pattern of quartz after heat treat-:ment. Reflection method, with 25-kV. electrons

/by virtue of a more open structure formed because of the less drastic method of generation.

3. The effect of polishing on the solubility of a silica dust is greatest for a massive crystalline substrate, next for a dust with the transitional layer of cryptocrystalline silica present and least for an amorphous surface.

4. Solution and sorption properties of three silicious dusts were found to be enhanced by the generation of a disturbed layer on the particle surfaces by polishing, just as such properties are less marked on removal of the disturbed layer produced by grinding. Vitreosil is assumed to be wholly amorphous, but exhibits an increase in equilibrium adsorp-:tion of Methylene Blue on production of a disturbed surface layer by polishing - an increase much larger in extent than the decrease with which removal of the disturbed layer is attended. This would again seem to indicate that the polished surface on fused silica particles is of a more open structure than the disturbed layer formed by grinding.

5. The results of the electron-optical examination provide strong confirmatory evidence for the concept, outlined by chemical methods, that the disturbed layer on polished crys-:talline and amorphous silica is virtually identical with the disturbed layer produced by crushing and grinding operations. Slight fragmentation of particles of the polishing agent occurs during the formation of the former type of layer, but this is only a very minor effect.

/6. It is possible to reduce the solubility of samples of polished quartz and untreated vitreous silica by severe heat treatment. The change in solubility is accompanied by partial recrystallisation of the surface layers of both materials. Since the polish layer is thus capable of devitrification, strong evidence is provided by this result for the amorphous nature of the disturbed layer produced by polishing.

7. A similar result was observed with the disturbed layer on finely ground quartz particles. The solubility is mar-:kedly reduced by heat treatment, but the extent of recrys-:tallisation of the disturbed layer on the particle surfaces, though quite definite, is rather smaller than would be expec-:ted on the basis of the solubility figures. The process is of little use at present in completely devitrifying a sample of ground quartz or Vitreosil, so that the silica content may be estimated by the technique of differential thermal analysis.

SUMMARY OF CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

1. The nature of the disturbed layer.

The surface layer on a particle of finely ground quartz or Lochaline sand is amorphous. This conclusion can be regarded as the logical termination of part of the investi-:gation commenced in these laboratories by Clelland and Ritchie[55], who established the presence of this layer of highly soluble silica on the surface of silicious dust particles produced by crushing and grinding.

There is also evidence in the foregoing work for the presence of a layer of cryptocrystalline silica between the disturbed layer and the truly crystalline core of a crystalline silica particle. The presence of this transitional layer can be explained in the light of results obtained by Clelland et al.[54] who showed that the dissolution of silica (mainly in the colloidal form) from the particle surfaces took place gradually, the initial high solution-rate falling slowly to a low equilibrium value. This result alone points to the con-:clusion that the disturbed layer is not discrete; coupled with the findings of the present investigation it shows that the gradual reduction in solution-rate of a silicious dust can be ascribed to the presence of the transitional layer, whose solubility must lie between those of the disturbed layer and the crystalline core.

Since it is known that silicic acid is very reactive in producing experimental silicosis, it is tempting to predict the results of animal experiments utilising silica dusts with /

/and without the disturbed layer, and to postulate that removal of the layer (by buffer solution or hydrofluoric acid) will markedly reduce the toxicity as well as the silica solubility. Experimental evidence, however, does not support such a hypo-:thesis. It has been shown by King, Mohanty, Harrison and Nagelschmidt[105] that although removal of the disturbed layer from a quartz dust reduces its silica solubility to 10% of the original value, it had no effect on its pathogenic pro-:perties. Removal by treatment with HF, however, markedly increased the pathogenicity. It would seem that there is no correlation between the silica solubility of a dust of this type, as determined in vitro, and its fibrogenic effect in animals, and that the disturbed layer is not the causative agent in the production of fibrous tissue.

It is suggested, however, that in experiments of this nature the mode of removal of the surface layer is of paramount importance, and biological inactivation of the particles may have occurred during the leaching process, or enhanced activity obtained by ion adsorption from hydrofluoric acid. Further work might profitably be directed towards the clarification of such in vivo reactions particularly in the case of a dust treated with hydrofluoric acid, and to obtaining a less vigorous method of removing both layers. The transi-:tional layer may be of great importance in such experiments; it has been shown in the present work that the silica solu-:bility of a Lochaline-sand dust was reduced to ca. 50% of /

/its original value by leaching with buffer solution for 8 weeks. Electron-optical results indicated the presence of the transitional layer. The longer period of leaching used by King et al.[105] (22 weeks) may have been successful in removing the transitional layer so that it has not yet been critically examined. It seems necessary to have an electron-optical picture of the state of the particle surfaces while attempting correlation between solubility and fibrogenic properties.

2. The effect of acids on the solution and sorption properties of silicious dusts.

It is obvious from the results of this investigation that we must recognise the importance of the pre-treatment of a mineral dust with acid, in preparation for determination of silica solubility or for use in the production of experimental silicosis. The results of such experiments cannot be accepted without reserve if the dusts in question have been purified by treatment with mineral acid. It is also possible that the estimation of free silica in such dusts will provide erroneous results.

In order that the mechanism of the reaction be fully established, it will be necessary to identify elemental hydro-:gen liberated from the surface of an acid-extracted silicious dust (e.g. Lochaline sand, DRC silica, olivine) during heat treatment; this will be an extremely difficult analytical experiment, but possibly conversion to water and detection by the Karl Fischer reagent would be a feasible route.

/ The presence of the disturbed layer on silicious dust surfaces is very important in sorption, as well as in solution processes. The activity of the layer in adsorption experiments is, perhaps, worthy of more extensive research since it is possible that pathological changes in lung tissue may result from the adsorption of organic materials (e.g. amino acids, proteins).

The same anomalous result is apparent in sorption processes as was obtained by Clelland et al.[54] in solution processes. Since Vitreosil is assumed to be wholly amorphous, the removal of the disturbed layer would not be expected to result in altered adsorption properties. The equilibrium adsorption of a basic dyestuff (Methylene Blue), however, is reduced after etching vitreous silica particles. The acti-:vity of this surface layer on fused silica particles has been ascribed to physical differences in the structures of the amor-:phous core and the disturbed layer. The results of Part lll are in agreement with this concept.

The effects of acid extraction and heat treatment of an acid-extracted dust on the adsorption of Methylene Blue were investigated with the object of adding precision to the results which indicate that mineral acid extraction of impure silicious dusts increases their silica solubilities by forming a layer of adsorbed hydrogen ions on the irregular surfaces produced by removal of impurities. Results of these sorption experiments support this concept. A thorough investigation of changes in /

/solution and pathogenic properties of a large number of sili-:cious dusts, by extraction with mineral acid, would clearly aid further in establishing the exact nature of the reaction, and add precision to the solubility theory of silicosis.

3. The effect of polishing on the surface structure of silicious dusts.

It has been shown that the highly soluble surface layer generated on silica dust particles by polishing with an abrasive is very similar to the disturbed layer produced by crushing and grinding operations. Using the technique of electron diffraction, this layer (also called a disturbed layer) has been shown to be amorphous. Again the apparently anomalous behaviour of fused silica particles is evident in that such a dust exhibits an enhanced solubility on production of a polish layer on the particle surfaces. It is thought that the structure of the layer is more open than that of the core. Some particles of polishing agent were shown to be fragmented during the polishing process.

Although the results of this part of the work may not have the practical significance of those obtained in the previous sections, it is thought that they might offer a suitable alternative to the line of research suggested in (1) above, where it was stated that removal of the disturbed layer from silicious dust surfaces with hydrofluoric acid might produce an activated surface by virtue of adsorption from the acid. The preparation of suitable dusts without the disturbed/

/layer may thus prove a difficulty in assessing their true fibrogenic properties. Since the disturbed layer pro-:duced by polishing is very similar to that produced by grinding and can be generated on finely ground silica, the true effect of an amorphous surface layer may be found by determining the pathogenicity of a silica dust after removal of the disturbed layer by treatment with borate buffer solu-:tion and again after polishing with a rock crystal polishing agent. Although this does not eliminate the necessity for leaching with a buffered solution (to remove the layer pro-:duced by grinding), the polished surface is known to be very active in solution and sorption processes and if the assumption that it has a very open type of structure is correct, it may exhibit a greater fibrogenic effect than the core, or the disturbed layer.

4. Possibility of recrystallisation of the amorphous surface layer on silicious dusts.

The estimation of the true silica content of dusts plays a major role in the field of silicosis research, and this experimental work was undertaken with the aim in view that it may be possible to utilise the technique of differen-:tial thermal analysis for the estimation of amorphous silica (after devitrification by heat) as well as of crystalline silica. At present, however, the method is of little use in recrystallising the amorphous layer although the reaction does

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/occur to a minor extent. Future work might profitably be carried out by the addition of materials (as fluxes) to cata-:lyse the change, or possibly by the use of much higher tem-:peratures since silica is a very stable substance. It would also be advisable to estimate the silica content of each heated sample by differential thermal analysis, as well as to record electron-optical effects, in order to obtain a much clearer picture of the extent of the recrystallisation.

Furthermore, success in this direction would lead to an ideal method of demonstrating the fibrogenic properties of an amorphous surface layer since it would be possible to assess these properties before and after devitrification. This would also eliminate the necessity for removal of the disturbed layer by chemical methods.

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